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The effect of ionic exchange upon the engineering properties of soil

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Rensselaer Polytechnic Institute

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THE EFFECT OF IONIC EXCHANGE
UPON THE ENGINEERING
PROPERTIES OF SOIL

George J. Cooper

COOPER

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THESIS
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Letter on front cover:

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SOIL

George J. Cooper

THE EFFECT OF IONIC EXCHANGE

UPON THE

ENGINEERING PROPERTIES OF SOIL

Submitted to the Faculty of

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In Partial Fulfillment of the Requirements

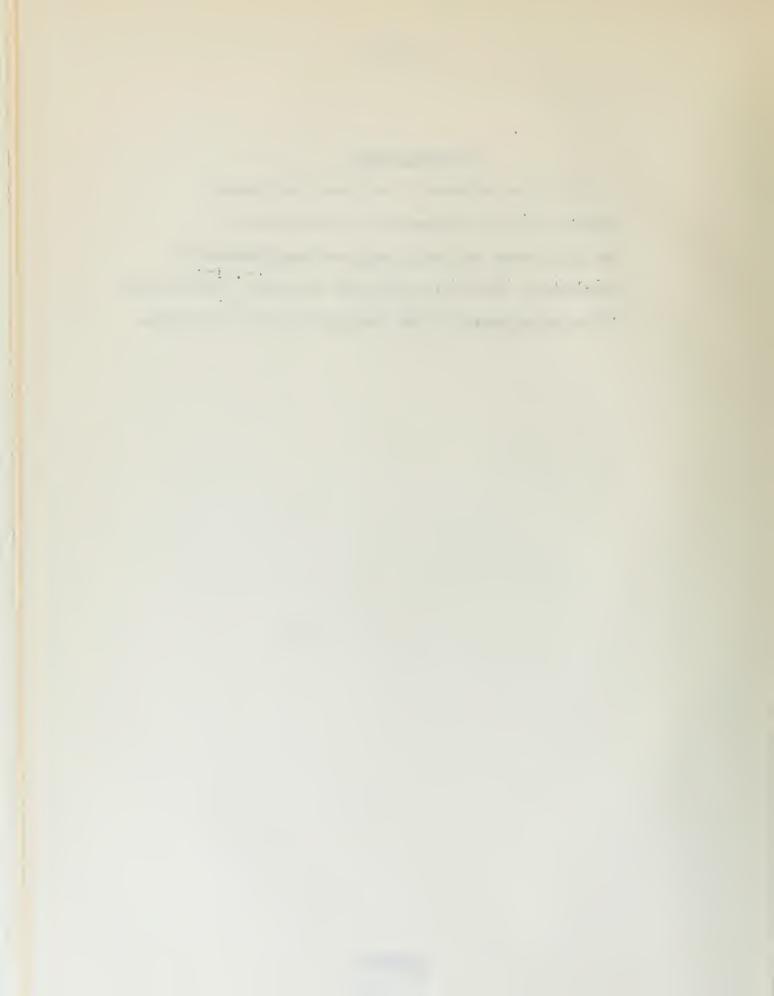for the Degree of

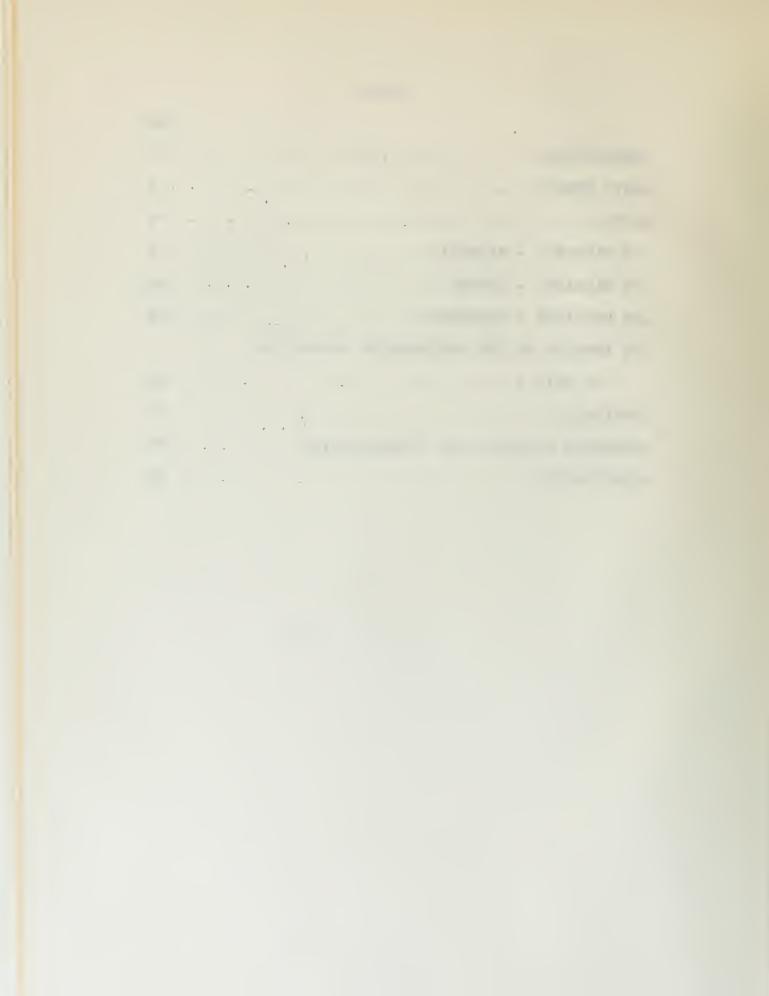Master of Civil Engineering

by

George J. Cooper

May 1954

ACKNOWLEDGMENT

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INTRODUCTION:

The property of ion exchange and exchange reaction mechanisms in soil are of great fundamental and practical importance to the engineer concerned with the use of soil as an engineering material. This property of soil has been little understood and consequently neglected by many engineers in the past. In the past 20 years of rapid growth of the field of Soil Mechanics the greatest emphasis has been placed upon determination of more or less "physical" characteristics of soil masses such as shear, compaction, swelling, gradation, frost heave, permeability, stability, durability, consolidation and other properties intimately connected with use of the soil in engineering. This investigation of physical properties was, is, and will continue to be a necessary part of the field of soil mechanics; however, concurrently with such an investigation a study of the fundamental properties of the soil responsible for the physical engineering properties must be carried out. A survey of soil mechanics literature will indicate that this phase of the field has been, to a large extent, neglected.

Current literature indicates that the importance of the fundamental properties of soil in engineering is being emphasized as it is recognized that only in this approach can the "physical" properties be fully understood and better use made of the soil in engineering.

Investigations of the basic properties of soils have been carried on for many years by agriculturists, ceramicists, mineralogists and physical chemists. The results of these investigations can provide much of the basic information necessary to provide a more clear understanding

of the underlying factors affecting the engineering properties of soil.
This information can also suggest many specific investigations necessary
to determine more fully the exact effect of various factors on soil
behavior in engineering practice.

This thesis is an attempt to correlate and evaluate the results of
investigations already made on the subject of the effect of ions on soil
properties. This correlation would normally be made in preparation for
an extended program of research into the subject. Time does not permit
the following up of the results of correlation by actual laboratory in-
vestigation, however, the various outlines of research necessary will
perimit this to be done intelligently in the future. Undertaking a
particular line of investigation in ion exchange without adequate know-
ledge of techniques, previous work, and underlying theory would result
in erratic results subject to misinterpretation. It will be noted, in
reference to various work previously performed, the pitfalls and mis-
interpretation which can result from inadequate knowledge.

BASIC THESIS:

The basic propostion is offered, and herein defended, that ions within a soil mass influence the engineering properties of the soil mass to varying degrees. The degree of influence is dependent upon factors within the soil mass which will be herein examined. The term "ions" shall include cations and anions, both inorganic and organic. The organic ions shall include those organic compounds which are not "ions" in the strict sense of the term but exhibit properties of ions. The term "soil mass" shall include all loose mineral grain aggregates above the rock mantle of the earth, together with any natural material, inorganic or organic contained in these aggregates. "Engineering properties" of the soil mass shall be any property which will in any manner affect its use as an engineering material.

It is a primary aim of this thesis to clearly demonstrate the basic fact that ions influence the properties of soil before and during soil formation, and thruout the history of the soil, until final use as an engineering material.

SCOPE:

In order that the relationship of ions to soil may be more clearly understood, all phenomena in any way connected with these relationships must be presented and examined. As will be pointed out, in a natural soil mass the factors which may have a bearing on the type of ions present, and their relation to the soil, vary widely and must be carefully determined and evaluated for each particular soil.

The genesis of soil masses, soil decomposition factors, basic composition and variations in composition of the pertinent soil minerals, will be presented and possible effects on ionic phenomena discussed.

The physical characterisitcs of soil constituents, such as particle size, shape of particle, effect of specific surface of particles and soil structure, are intimately correlated with ionic phenomena and will be considered in connection with the particular phases with which they are concerned. Water - soil relationships are partially considered in this category also.

The various theories of ion exchange and development of these theories must be presented and examined for possible explanation of the mechanism of ionic phenomena.

Data resulting from investigations of ionic enchange is correlated with ionic exchange mechanism theories in an analysis and examination of the validity of these theories.

The specific results of various investigations of ionic effects upon the physical properties of soils are presented and analysed in an attempt to present a coherent picture of possible trends in the effect

of ions upon the engineering properties of soils.

Specific projects of investigation will be delineated which are desirable and necessary to further improve the understanding of ionic phenomena, which have a direct bearing upon the use of soil as an engineering material.

Comment will be made upon various investigations concerned with the stabilization of soil masses by artificially induced ionic reactions.

A short prognosis of future possible practical applications of ionic mechanisms to improve soil properties will be attempted.

The bibliography resulting from this investigation will provide many references of. factors affecting ionic phenomena which will assist future investigators engaged in a necessary extension of this attempted correlation and work herein suggested.

ION EXCHANGE - GENERAL

The relationship of ions to soil has been a subject of investigation since 1845 when Thompson, and later Way, in 1850, investigated the adsorption of ammonia by soil. Kelley (1948) has presented an excellent historical resume of cation exchange and the development of exchange theories.

Way discovered in his early investigation of soil and ions that the clay in soil was primarily responsible for ionic exchange. The clay minerals in soil, and to a much lesser degree, the sand and silt have the ability to adsorb certain cations and anions and retain them in an exchaneable state. The ions held on a soil particle in an exchangeable position can be removed and exchanged for other ions by treatment of the soil with an aqueous solution of the other ion. The exchangeable ions are adsorbed around the outside of the mineral structural unit and normally do not affect the mineral crystalline structure itself.

The commonest exchangeable cations in soil are, in general order of relative abundance, Ca, Mg, H, K, NH_4, and Na. The most common anions in soil are SO_4, Cl, PO_4, and NO_3. In addition to those above, other ions which may be present, but normally not as exchangeable ions, are iron and aluminum in the form of free oxides. Organic ions and anions derived from decomposition of organic matter are present in most soils and may have a great effect upon ion exchange.

These will be discussed more or less separately from consid-
erations of inorganic ions.

The property of exchange capacity, often called base-
exchange capacity, is measured in terms of milli-equivalents
of ion per gram of soil, or more commonly per 100 grams of
soil. When referred to in this paper, milli-equivalents will
be commonly abbreviated to: m.e./100 gms soil.

$$\text{ion exchange expressed in milli-equivalents} = 1000 \times \frac{\text{weight of substance in grams}}{\text{chemical equivalent weight of substance}}$$

The term ion exchange is preferred, rather than base exchange,
since H is involved in cation exchange and other exchange
involves anions or organic ions.

In order that the factors involved in ion exchange may
be considered in an orderly manner, we shall consider first,
the ion exchange material and source of attraction; second,
ion exchange theories; and last, the manner of exchange of
various ions.

ION EXCHANGE - MATERIAL

The sciences of geology and agriculture have contributed the result of much research which has immeasurably increased our understanding of the formation and mineral structure of our basic material - soil.

Jeffries (1947) briefly discusses the general mineralogical composition of the earth's crust and the primary mineral sources of clay minerals. Grim (1953) presents an excellent survey of literature pertaining to the origin and occurrence of clay minerals. Although the earth's crust is essentially igneous, the surface of the crust, in which we are primarily interested, is underlain by 75% sedimentary rocks and only 25% igneous rocks. In most cases, therefore, soils have been derived generally from pre-existing sediments and metamorphic rock and are a part of the cycle of weathering which started with igneous rocks, and minerals of which igneous rocks are made. Minerals may be classed as primary minerals, which are formed by solidification of molten magma, or secondary minerals formed as alteration or decomposition products of primary minerals. In the study of soil, we are concerned with the secondary minerals and as will be demonstrated later, in particular, the clay minerals.

Clark (1924) presents an estimate of the percent of various mineral constituents in the earth's crust, and sediments in the crust up to a depth of 10 miles.

MINERAL COMPOSITION OF CRUST AND
AVERAGE SEDIMENT OF THE EARTH

MINERAL	CRUST %	AVERAGE SEDIMENT %	AVERAGE SEDIMENT CARBONATE FREE %
Feldspar	57.8	7.0	8.7
Quartz	12.8	38.0	47.5
Amphibole	16.0	--	--
Mica	3.6	20.0	25.0
Accessory	8.0	3.0	3.8
Clay	1.1	9.0	11.2
Carbonates	0.5	20.0	--
Limonite	0.2	3.0	3.8

As will be noted from the above table, the feldspar groups, both alkalic and plagioclase, are the most abundant and consequently, the most important in our soil studies. The feldspars are found in all horizons of most soils. The feldspars are the source of large amounts of K, Ca, Ba, Al, and clay minerals as a result of their decomposition.

The amphiboles contribute alteration minerals which are generally considered part of the clay mineral family, the palygorskite series. This series, which includes attapulgite and sepiolite, has not been thoroughly investigated. The amphiboles also contribute Ca and Mg ions.

The mica minerals contribute high amounts of K ion to the soil from the muscovite series, upon weathering. The mica minerals contribute the hydrous mica clay minerals of which illite is the largest member. Chlorites may be derived from mica primary minerals. The mica minerals are both primary and secondary.

The accessory minerals contribute little to the clay mineral series, but may in certain cases, contribute ions of minor importance, because of small amount and effect, except in special cases, such as Mn, Li, Ba, Ti, P.

The clay minerals in the table are both products of weathering, and hydrothermal alteration.

The carbonates contribute Mg, Ca and Ba and are the cementing agent, upon crystallization, in many soil deposits.

Limonite contributes Fe which may have important effects as will be noted later.

In general, clay minerals are produced by a weathering process of igneous, sedimentary, or metamorphic rock or by hydrothermal action altering adjacent rocks directly into clay minerals. The weathering process produces the largest percentage of clay mineral deposits, although the hydrothermal type of deposit cannot be overlooked since large deposits of one type of mineral may be produced in a relatively small area. Basically, all secondary minerals are produced as a result of ionic exchange and rearrangement. The action in hydrothermal production is fairly rapid, while in weathering, the action is slow, geologically speaking. Grim (1953) references the work of Correns and Englehardt whose work indicates that weathering proceeds by the breakdown of parent material to ionic solutions and that secondary minerals are reaction products of such ionic solutions.

Grim(1953) also references Niggli whose work indicated that
under certain conditions feldspar reaches a colloidal state
before formation of secondary minerals.

The formation of clays by hydrothermal action is well
covered by Grim (1953). Clays formed by hydrothermal action
may be any one of the clay mineral family except palygorskite.
The type of clay mineral formed depends in large part upon the
acidity or alkalinity of the hydrothermal solution. The
important hydrothermal clay deposits in the United States
are in the West.

The type of clay mineral deposit formed from weathering
depends upon several factors. The parent rock material of
the clay soil determines to some extent the type of clay
formed, but other factors have a greater influence. Both
kaolin and montmorillonite may develop from the same parent
material under the influence of other factors. The alkali
content of the parent rock is the main factor influencing
the ultimate clay mineral. Rocks containing no alkali
minerals can develop only a kaolin clay unless moving ground-
water brings in outside alkalis.

The climate to which a soil is subjected during its
formation and life history has the greatest influence upon
the type of soil and clay mineral formed. Briefly, in a
region of high rainfall and warm temperature, the products
of the soil would be leached from the upper zones and perhaps

concentrated in lower zones in the soil profile. In a soil
subjected to only moderate rainfall, the decayed mineral
products would not be removed from the upper zones. The
affect of the climate upon the type and abundance of vege-
tation determines the amount of organic matter and the
degree of decomposition of organic matter in the various
soil profile layers.

On the basis of climate, soils are classed into Great
Soil Groups of the World. The following table adapted from
Lyons and Buckman (1943) gives a general idea of the means
of classification.

GREAT SOIL GROUPS OF THE WORLD

I.   Zonal Humid Soils

    A.   Tundra

        1.   Gray peaty accumulation over various
           mineral horizons. Substratum and often
           subsoil perpetually frozen. (Arctic soils)

    B.   Podsolic

        1.   Formed in cool humid climate. Bases leached
           out soil generally acidic. Forms large part
           of northern New England and northern Lake
           States.

    C.   Lateritic

        1.   Formed in humid tropical climate. Bases
           dissolved. Iron and aluminum concentrated.
           Soil generally alkaline or neutral. None
           formed in United States recently.

    D.   Intrazonal Groups

        1.   Gradations between above groups.

II. Zonal Aridic Soils

    A. A variety of basic aridic soils in this group
       differing in formation by amount of rainfall.

    B. Intrazonal Groups

      1. Gradations between basic zonal groups.

Each of the zonal groups and sub-groups is characterized
by general properties. For example, (Grim, 1953) the red and
yellow podsolic soils all contain only kaolin or predominately
kaolin as a clay mineral. The other various groups also indi-
cate the formation of predominate types of clay minerals as a
result of the type of weathering to which they have been
subjected. The various soil groups also have other predom-
inate characteristics such as pH range, and most important,
certain ion concentrations.

Grim (1953), Lutz and Chandler (1946), Clark (1924),
Lyons and Buckman (1943), Glinka (1927), Kelley (1951),
Robinson (1914), U.S.D.A. Yearbook 1938, and other U.S.
Department of Agriculture, Bureau of Soils, publications
contain excellent sections on the development of soils and
characteristics resulting from the mode of development.
Extensive bibliographies on soil formation are contained in
the above publications also.

Nikiforoff and Drosdoff (1943) have made an excellent
analysis of the genesis of a claypan soil. Of interest in
this analysis is the building up of silt fractions in the
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analysis of the genesis of a claypan soil. Of interest in
this analysis is the building up of silt fractions in the
soil from complete decomposition of parts of the clay

fraction resulting in a recombination of the released silica with existing silt, in certain horizons. Also of interest from an ionic standpoint is the formation of typical clay-pan concretions, of a complex nature, from free iron and manganese. This reversal of the weathering process, a building up of minerals from decomposition products has been noted by Hardy (1939) and Alexander (1941) also.

Other factors influencing the type of soil and clay minerals produced are the topography of the land influencing water tables, the mode of transport and deposition of material moved from its parent material site, and the type of parent rock or other material upon which the transported material is deposited.

A greater recognition, by the soil mechanics engineer, must be given to the genesis of soil groups and the characteristics of the groups and sub-groups. That such recognition is being realized is indicated in the recent interest by highway engineers in the use of soil type maps in planning highways. Bulletin No. 22, "Engineering Use of Agricultural Soil Maps" (1949), published by the Highway Research Board of the National Research Council is an example of the trend. This publication contains a partial bibliography of other recent literature on soil types applied to engineering. The soil engineer who is familiar with the soil groups and series and the general characteristics of each, such as clay

minerals, ions present, soil structure and mode of forma-
tion, will have a much better understanding of a particular
soil and will be better able to predict its action than one
who depends solely upon laboratory tests.

Noted under projects for investigation is one pertain-
ing to soil group characteristics. The clay minerals, whose
presence determine many of the most important engineering
properties of soil must be considered in some detail.

Basically, all clay minerals are aluminum silicates
of definite crystalline structure. Pauling (1930) began
the investigation of clay mineral structure and other
mineralogists have since contributed very complete material.
Grim (1953) and Kelley (1948) give very complete biblio-
graphies on clay mineral structure investigations.

Various general categories of clay minerals have been
in use in the past but the development of structure since
1930 has resulted in general acceptance of the classes of
kaolinitic, montmorillonitic, and illitic minerals. Actually,
illite is structurally similar to montmorillonite.

The following table of clay mineral classification is
modified from Grim (1953). The mineral shape and size are
from Brindley (1951).

Classification of Clay Minerals

I. Two layer minerals - Sheet type structures composed
   of units of one layer of silica tetrahedrons and
   one layer of alumina octahedrons.

A. Equidimensional

    1. Kaolinite group

        a. Kaolinite - Hexagonal plates, variable
           thickness, 0.1 to 3 microns, often
           poorly defined.
        b. Nacrite -
        c. Dickite - Well defined hexagonal
           plates, 1 to 10 microns.
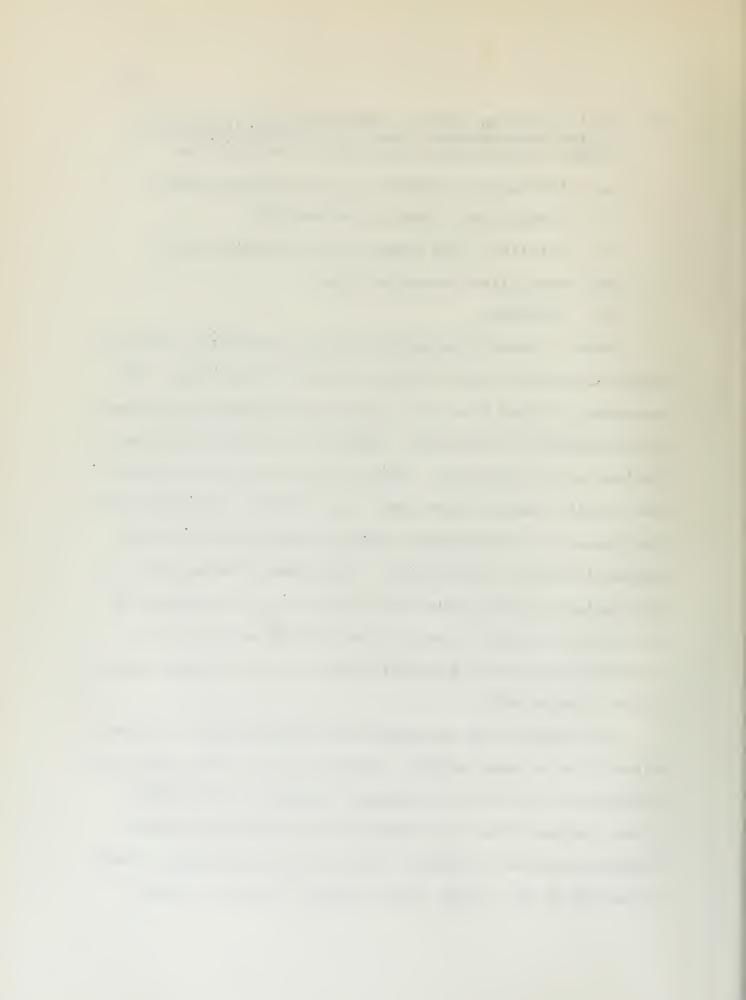
B. Elongate

    1. Halloysite group - Elongated rods or tubes,
       some tubes split open and unrolled. Length,
       0.1 to 1 micron, tube diameter, 0.05 to .2
       microns.

II. Three layer minerals - Sheet structures composed of
    two layers of silica tetrahedrons and one central
    dioctahedral or trioctahedral layer.

    A. Expanding lattice

        1. Equidimensional

           a. Montmorillonite - Poorly defined,
             hexagonal, less than 1 micron.
           b. Sauconite
           c. Vermiculite

        2. Elongate

           a. Montmorillonite
           b. Nontronite - Lath like or ribbons
           c. Saponite
           d. Hectorite - Lath like, 1 micron long,
                      0.1 micron wide.

    B. Non-expanding lattice

        1. Hydrous mica or illite group - glauconite,
          Allevardite - Poorly defined, hexagonal
                 flakes or ribbons, 1 micron
                 size.

III. Regular mixed layer groups - ordered stacking of
    alternate layers of different types.

    A. Chlorite group

IV. Chain structure types - Hornblende-like chains of silica tetrahedrons linked by octahedral groups of oxygen and hydroxls containing Al and Mg ions.

    A. Attapulgite - Fibers, 0.1 to 5 microns long

    B. Palygorskite - Same as attapulgite

    C. Sepiolite - Rod forms 0.1 to 5 microns long

V. Non-crystalline amorphous clays

    A. Allophanes

Group I above is generally called kaolinites, Group II, montmorillonites, and illites considered separately. The presence of Group V is not clearly established and further investigation is necessary. Group IV is still not clearly defined as to structure. Within each of the above groups, one specific mineral may grade into another, depending upon the degree of isomorphism. This is particularly true of montmorillonites and illites. The mineral "beidellite" is not included in the above list since it is established by the recent work of several investigators that this is a mineral variation of montmorillonite, due to slight isomorphism. (Grim 1953)

The oxygen atom determines the configuration of clay minerals to a great extent. Because of its large size, 1.40 angstroms (1/10,000 of a micron), compared to the other atoms, oxygen forms the "skeleton" of which the mineral crystal structure is built. This is not surprising, considering 95% of the volume of the earth's crust is oxygen.

From the foregoing classification, it is noted that
the minerals are formed of "sheets" of silicon and alumina.
The silicon sheet is formed of "tetrahedrons", composed of
basic units made up of a Silicon atom (ion) surrounded by
four large oxygen atoms. Adjacent silicons share oxygens,
that is, each two silicon ions share one oxygen atom which
is common to two tetrahedrons. The alumina "sheet" is made
up of "octahedrons" in which each aluminum (ion) atom is
surrounded by six oxygen atoms. Oxygen atoms are shared by
the aluminum atoms. One of the fundamental factors to remem-
ber in the structure of the clay minerals is the space avail-
able between the oxygen atoms in each unit tetrahedron and
octahedron. This available space determines which other ions
can replace either silicon or aluminum ions. It is this
geometrical spacing of the ions in the crystal lattice which
accounts for many of the clay mineral variations and proper-
ties. In the case of the tetrahedron, the oxygen ions are
stacked like a pyramid of cannonballs with three ions in one
layer touching each other, and the fourth ion on top of these
touching the other three. The space under the top ion at the
apex of the pyramid is occupied by the silicon ion. On the
basis of oxygen crystal ionic radii being 1.40 Angstroms,
the space available for the silicon ion is about 0.55 Ang-
stroms. The silicon ion has a diameter of about 0.39 Ang-
stroms, which is the closest ion size to the available

space and very abundant. The tetrahedron can be considered
most closely bound together with the silicon ion since this
would bring the centers of all ions closest together. Other
ions, such as boron (0.20A.) have a smaller diameter and may
enter into the crystal lattice, but do not provide as close
a relationship since they are too loose a fit, so to speak,
and the valence is less. As will be noted, larger ions may
replace the silicon, such as aluminum and iron, but these
have a lower valence (3) compared to silicon (4), and the
larger diameter does not tie the tetrahedron as tightly as
the silicon, hence they cannot replace the silicons except
in a few tetrahedrons.

The aluminum octahedron may be considered as two layers
of three oxygen ions, each layer arranged in a triangle with
ions touching. When upper and lower layers touch, the space
available in the center is about 0.61 angstroms. The alumi-
num ion is about 0.57 angstroms, which is a very close fit.
The aluminum is replaced at times with similar sized ions
such as iron (0.67 A) and magnesium (0.65 A). The oxygens
are partially replaced with hydroxl ions. This does not dis-
rupt the close packing, since the hydrogen is of small size
and fits in space available.

The crystal structure of the kaolinite group minerals
is composed basically of one tetrahedral silicon sheet and
one octahedral aluminum sheet. The tetrahedral sheet is

placed so that the apex of the pyramid is down toward the octahedral sheet, and the oxygen atom at the apex is shared by both tetrahedron and octahedron. This basic layered structure of two sheets leaves a layer of oxygen ions on one face and a layer of hydroxl ions on the other face. The hydroxl and oxygen layers of adjacent layer structures are attracted strongly, resulting in a very stable crystal composed of alternate octahedral and tetrahedral layers, bonded by the H in (OH). In the halloysite member of the kaolinite group, Grim (1953) indicates that Hendrichs (1938) and others believe that there is a molecular layer of water between the adjacent kaolinite layers of tetrahedral and octahedral faces. This water layer is believed to have a definite configuration or structure between the tightly bound kaolinite layers.

The structure of kaolin indicated above was first outlined by Pauling (1930) and later developed by Gruner and revised by Brindley, as indicated by Grim (1953).

The kaolin crystal is essentially electrically neutral; that is, the valences are satisfied within the structure. Considering the basic two layer unit, the charge distribution is as follows:

6 O--	12 -	(Top oxygen layer)
4 Si	16 +	
4 O & 2 (OH)	10 -	(layer common to tetrahedral and octahedral sheets)

$$4 \text{ Al} \qquad\qquad 12 +$$
$$6 \text{ (OH)} \qquad\qquad 6 -$$

The structural formula is $(OH)_8 \ Si_4 \ Al_4 \ O_{10}$.

There is some evidence that in poorly crystallized kaolin there is a slight substitution of titanium or iron for the aluminum in the octahedral unit.

In silicon rich kaolins, Hendricks (1942), suggests that two tetrahedral layers are joined together at the apex and that this silicon rich layer unit is interlayered between standard kaolin layer units.

The montmorillonite group mineral structure, as indicated by Grim (1953), was first proposed in 1933 by Hoffman, Endell and Wilm, and later modified by Marshall (1935) and Hendricks (1942).

The basic layer unit is composed of two silica tetrahedral sheets with one aluminum octahedral sheet between. The apex of the tetrahedrons point inward and lie in the same plane as the (OH) in the octahedron sheet. Ions shared by both tetrahedral and octahedral sheets become O instead of (OH). When the unit layers are stacked in the crystal, the O layers are adjacent and hence the bond is weak, and there is good cleavage. It is important in the montmorillonites that water and other polar molecules do enter between the loosely bonded layers, between the unit structural layer, causing expansion of the lattice.

The theoretical balanced distribution of charges in the montmorillonite lattice is as follows:

```
6 O              12 -
4 Si             16+
4 O & 2 (OH)     10 -     (Layer common to tetra-
                            hedral and octahedral
                            layers)
4 Al             12 +
4 O & 2 (OH)     10 -     (Layer common to both)
4 Si             16 +
6 O              12 -
```

The theoretical formula is $(OH)_4$ Si_8 Al_4 O_{20} plus interlayer water.

Marshall (1935) and Hendricks (1942) emphasize that montmorillonite always differs from the above theoretical formula because of the substitution of ions within the lattice for the Al and possibly Si. This substitution of one ion for another in a crystal lattice is termed isomorphism. Possible substitutions are magnesium, iron, zinc, nickel, lithium, and others for the aluminum in the octahedral sheet, and substitution of aluminum and possibly phosphorous for silicon in the tetrahedral. The substitution of ions which are larger than the available space, such as Mg (0.65A) or Fe (0.67A) for Al, puts a strain in the lattice resulting in poor crystalline form of lath shape. The isomorphism in all montmorillonites results in poorly defined crystals as compared to the clear hexagonal definition of kaolin.

The total net charge in montmorillonites is always unbalanced. This unbalance is due primarily to substitutions

within the lattice. There is a negative charge unsatisfied
when Mg is substituted for Al in the octahedral sheet or
Al for Si in the tetrahedral sheet. In all octahedral sheets,
it is characteristic that only two-thirds of the possible
spaces are filled by Al ions since this satisfies the O and
(OH) valences. If Mg with a valence of 2 is substituted
for Al in the octahedral sheet, all spaces will be filled to
satisfy valency requirements. This increase in filled spaces
may tend to offset a deficit of positive charges in the tetra-
hedral sheets due to substitution of Si. The substitutions
tend to balance each other to some extent, but it has been
shown (Grim 1953) that a deficit of positive charges always
results. It should be noted that in the montmorillonites,
Fe does not replace Si in the tetrahedral layer.

In addition to the unbalanced charge in montmorillonite
due to replacement, a structural change has been suggested
by Edelman and Favejee (1940). This alteration in structure
suggested is the reversal of part of the silicon unit tetra-
hedrons in the tetrahedral sheet so that part of them have
the apex O in the outer layer instead of pointing inward to
the octahedral sheet. Further, part or all of these surface
O ions are probably replaced by (OH) ions. This would
result in a higher unbalanced net charge per crystal. This
supposition of Edelman and Favejee is not borne out too well
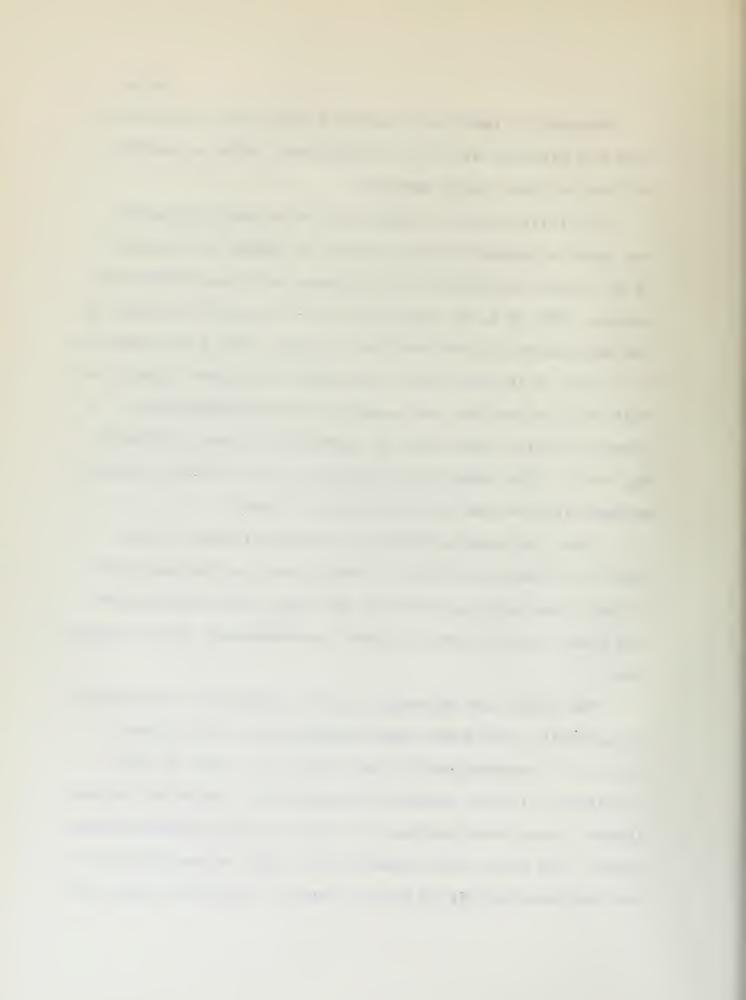by experimental results with X-Rays.

McConnell (1950) has suggested that some O tetrahedrons are replaced by (OH) tetrahedrons. This is possible, but has not been fully checked.

The illite series of minerals has a basic structure the same as montmorillonite except Si, which is replaced by Al in the tetrahedron, is balanced by K ions between the layers. This K is of such size that it just fits snugly in the depressions in the surface O layers. The K is bonded to 12 O ions, 6 in each layer, and holds the layers tightly so that the lattice does not expand as in montmorillonite. K between lattice layers may be partially replaced by Na, Ca, Mg, and H. The unbalanced charge is less in illite than in montmorillonite due to the K between layers.

There are many variations of montmorillonite which grade into those of illite. Transformation from one group to the other may take place if the right ions are present, and time is sufficient to permit rearrangement of the structures.

The other clay minerals, such as chlorite, vermiculite, palygorskite, and mixed layer minerals have structures similar to montmorillonite and illite, but vary in the stacking of layers, amount of isomorphism, and water between layers. Much work remains to be done on these miscellaneous types. The mixed layer minerals are inter stratification of the various minerals in the 2:1 lattice structure types and

are difficult to study.

This rather lengthy discussion of the soil minerals, clay minerals, their formation and structure has been necessary for two reasons. It has brought out the part played by ions in influencing the actual mineral composition of the soil, and most important, it has shown how the variation in mineral structure results in an unbalanced charge in the mineral crystals. This unbalanced charge and the location of the crystal lattice ions account for the variation in type and amount of ion exchange and will be referred to frequently in subsequent discussion of ion phenomena.
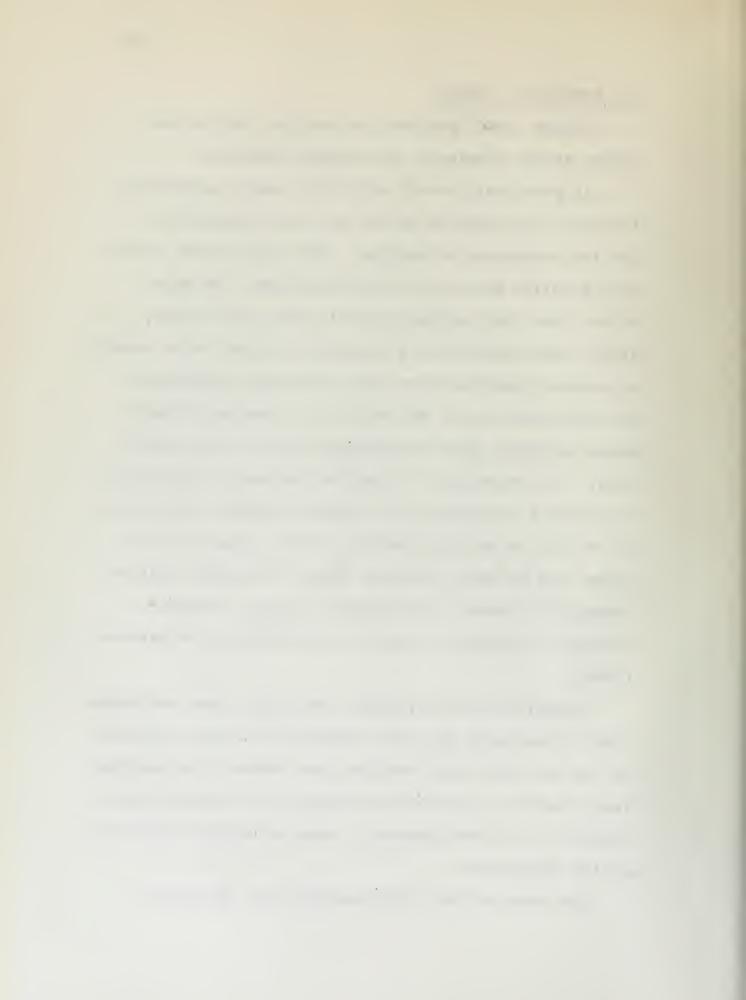
ION EXCHANGE - THEORY

Kelley (1948) presents an excellent historical resume of the prominent ion exchange theories.

As previously noted, Way (1850) early established that the clay fraction of the soil was responsible for the adsorption of cations. The exact nature of the clay fraction was not at that time known. In spite of the fact that various investigators early (1858, 1876, 1907) showed that crystalline minerals were capable of cation adsorption most soil scientists considered the clay fraction of the soil to be a series of amorphous collodial gels of aluminum and iron and silicic acid. The adsorption of ions was variously attributed to hydroget adsorption, Van Bemmelen (1888); adsorption of OH ions by the clay "particle" with adsorption of other ions on these, Wiegner (1925); colloidal zeolitic adsorption, Gedroiz (1912-1925); and the "acidoid" - "basoid", colloidal - chemical relationships of Mattson (1930).
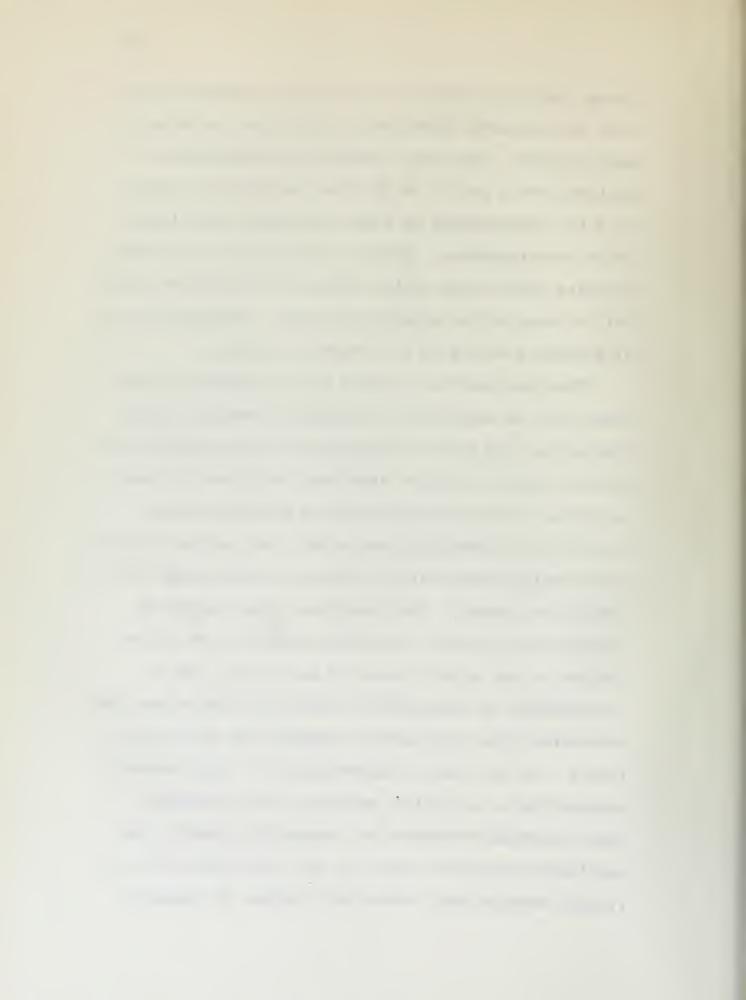
Hendricks and Fry (1930) and Kelley, Dore and Brown (1931) discovered that the inorganic colliodal material of the soil, the clay fraction, was commonly crystalline. This discovery placed ion exchange on a rational basis and led to the most generally accepted current theories of ion adsorption.

The work of the early investigators of ion ex-

change and their theories are not to be deprecated for
with the extent of knowledge at that time the theories
were rational. The very extensive investigations of
Mattson over a period of 20 years contributed a great
deal to understanding of ionic phenomena and triggered
other investigations. Mattson continually revised his
theories wheras many of his adherents did not and still
hold to many of his original concepts. Certain aspects
of Mattson's work will be referred to later.

From the previous section on clay minerals it was
noted that an unbalance of electrical charges existed
within the clay mineral lattice to varying degrees, de-
pending upon the lattice structure and degree of iso-
morphism. This unbalance resulted primarily from
unsatisfied valences of ions within the lattice structure
and normally results in an excess negative charge for the
lattice as a whole. This negative charge cannot be
considered as acting at specific points on the plane
surface of the crystal since in many cases, due to
isomorphism, the unsatisfied valence is deep within the
octahedral layer and must act through the tetrahedral
layers. In the case of isomorphism in a clay mineral,
montmorillmite or illite, which has the octahedral
layer sandwiched between two tetrahedral layers, the
unsatisfied negative charge or force may exert its in-
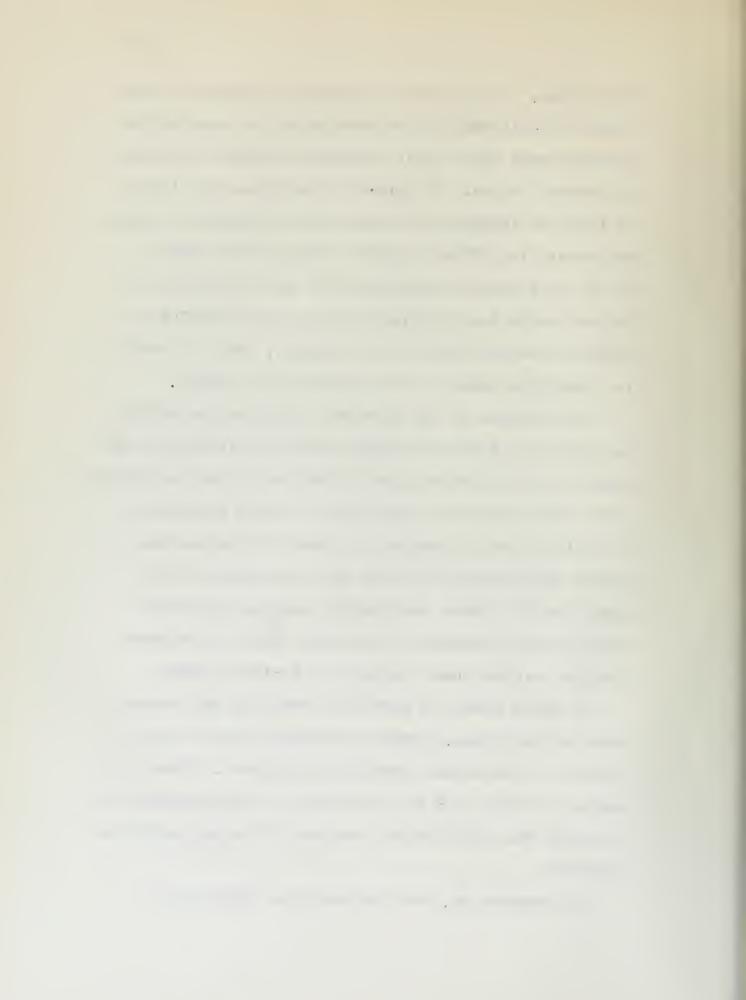fluence through both tetrahedral layers, in opposite

directions. In general, the minerals consist of many
layers of basic unit layer systems so the unsatisfied
valences must exert their influence through a distance
of several layers. In general, therefore, the "force"
or field of influence of each source of negative charge
may result in a "force field" acting at the surface
of the clay particle which will be more concentrated
in some spots due to reinforcement of the cumulative
effect of several unsatisfied charges. The net result
is a negative charge on the particle as a whole.

In addition to the negative charge on the particle
as a whole we have unsatisfied valences directly in the
surface of the particle due to OH ions in the tetrohedral
layer. The source of these ions as noted previously
is believed due to reversal of some Si tetrahedrons
within the tetrahedral layer and replacement of the
apex O by OH. These unsatisfied surface ions would
exert a more concentrated negative charge to attract
positive cations than the general particle charge.

A third source of particle charge is the broken
bonds at the edges, corners and broken sides of the
crystals of which the particle is composed. This
source of charge may be considered as fairly concentrat-
ed around the anion in the surface of the edge which is
"broken".

In summing up, the clay particle will have a

negative charge of varying size resulting from three
general sources; unsatisfied valences within the crystal
lattice, unsatisfied valences in the surface of the
particle due primarily to surface OH ions, and unsatis-
fied valences at the edges of the particle due to dis-
continuities in the crystal lattice layers.

The concept of location of the charges is usually
that the charge is a point charge. The author deprecates
this concept as narrowing the possibility of under-
standing the nature of the effect of the charges. The
true nature of the charge due to unsatisfied valences
is not known. It is preferred that the concept of a
spatial field of influence of the charges on all particles
be considered as a clearer picture of particle inter-
action. The size of this "sphere of influence" is not
known nor the distance from the source to which it
acts. Considering two oppositely charged particles we
know that the attractive force between the particles
varies as a function of the size of charge and distance
between the particles. Both van der Waals and Coulomb
developed mathematical expressions for this. Consider
further, however, that if two particles of equal charge
are attracted closely to each other, and theoretically
they satisfy each other, another particle may wander
close, due to random movement, and become attached to the
other two. One charge of the original two particles

is therefore shared among one of the original particles
and the newcomer. In effect this would reduce the
binding energy between the original two particles and
the total number of particles which could be held by
one charge would be a function of the size of charge
and distance between charge sources in conformance with
van der Waals - London concepts. This may (or may not)
however, demonstrate that a single charge may not be
completely satisfied by another single charge but exerts
a "sphere of influence". It is believed that if this
concept of a "field of force" is borne in mind it may
serve to help understand some of the ion phenomena
presented, particularly the effect of ions on clay parti-
cle water films.

Each of the three general groups of clay minerals
has a range of ion exchange capacity (expressed in
milli-equivalents) which is characteristic of the group.
Roughly the range for each main group is as follows
for the same particle size:

Kaolinitic	3 to 15 m.e/100 gms.
Montmorillonitic	60 to 150 m.e/100 gms.
Illitic	10 to 40 m.e./100 gms.

The ion exchange capacity of the kaolin group is
attributed primarily to "broken ionic bonds" at the
edges of the particles. The kaolin group has little
isomorphism and a stable structure. It is believed

there are few OH ions in the tetrahedral sheet due to
tetrahedron inversions.

The high exchange capacity of montomorillonites
can be attributed mainly to OH ions in the layer sur-
faces and general negative charge due to isomorphism
within the lattice. Adsorption of ions will take place
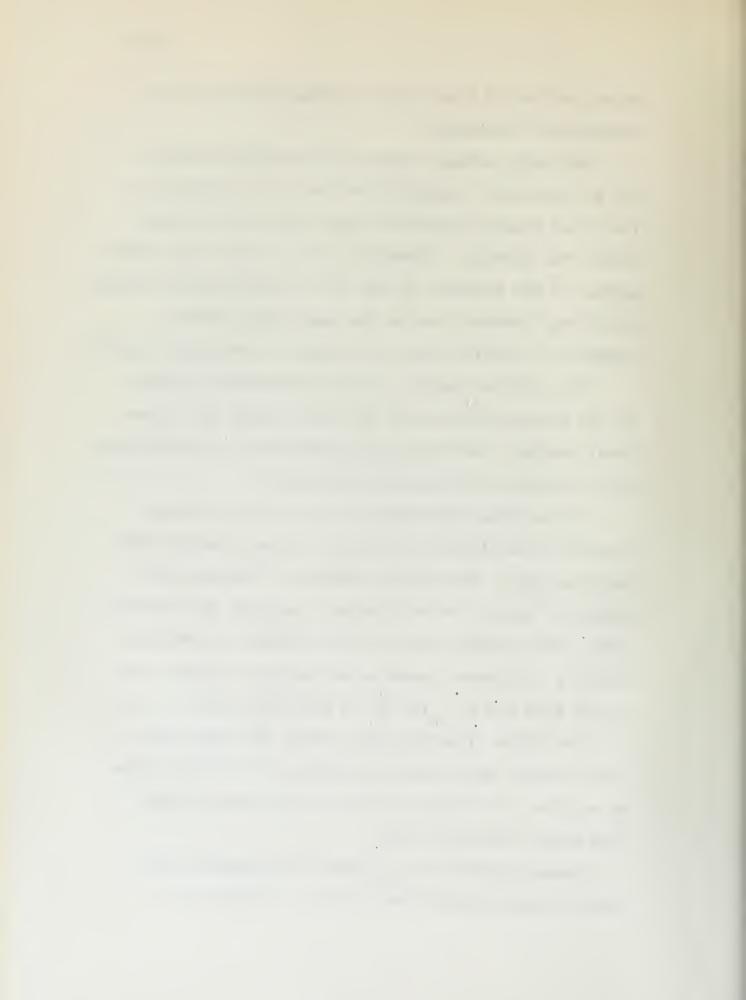mainly on the surfaces of the basal planes between layers.
This large surface area in the expanding lattice,
compared to particle size, accounts for the high capacity.

The illitic minerals are in between but similar
to the montmorillonites in that the charge and conse-
quent exchange activity is due primarily to isomorphism,
with adsorption on exposed basal planes.

It has been demonstrated that the ion exchange
capacity of kaolinite and illite minerals varies with
particle size. This would confirm the "broken bond"
source of charge for kaolins and, in part, for illites
also. Grim (1953) indicates that Harmon and Franlini
showed a consistent increase in exchange capacity for
kaolin from 2.4 m.e. for 10 to 20 micron size to 9.5
m.e for .05 to .1 micron size. Grim also indicates
that Grim and Bray showed an increase for illite from
20 m.e for .1 to 1 micron size to 41.7 m.e for the
less than 0.06 micron size.

Hauser and Reed and Caldwell and Marshall have
shown no appreciable increase in   exchange

capacity with reduction in particle size for montmorillo-
nites. This tends to bear out the surface adsorption
hypothesis. Any slight increase would be due to dis-
ruption of lattice layers exposing more surface.

The increase in illite is in part due to edge
bonds but more probably in large part to increased
accessibility of basal planes between layers.

Kelley and Jenny (1936) demonstrated that grinding
of clay minerals increased the exchange capacity of all
types. This would produce more basal plane fractures
in illite and montmorillonite, accounting for their
increase. Grinding tends also to completely destroy
the crystal structure if prolonged.

Having established the presence of a negative
field charge on the clay particles we should also note
the possibility of a positive charge. Thiessen (1942)
demonstrated by electron photomicrographs that negative
gold particles are exclusively adsorbed at the edges
of kaolinite. This positive attraction could occur
to a limited degree from exposed Al or Si at the edges
of broken crystal layer. This possible positive charge
would be small. The influence of the positive charge
may account for the limited anion adsorption which
takes place and may also account in part for some
structural orientation of fine clay particles.

Van Olphen (1951) has suggested that the positive

charges present on edges of particles may cause attraction between the edge and surface of adjacent particles thus accounting for certain of the structural relationships in clays.

It is well at this point to differentiate between the two types of ion exchange. In the majority of the references to ion exchange in this paper we will be referring to cation exchange which is the preferential adsorption of the clay particle for the positive valence ions in solution. Anion exchange refers to the adsorption of negatively charged radicals such as phosphate, arsenate, flouride, chloride, etc. As will be noted later, anion exchange is not as important as the cation exchange, except as it affects cation exchange capacity.

The exact relationship of adsorbed cations to the soil particle has been a subject of much debate. The most widely accepted current theory, particularly in the field of soil engineering, is that based upon the original mathematical theory of Helmholtz (1879). He proposed a double layer theory, derived from investigations, in which a layer of water dipoles is considered rigidly attached to the negatively charged surface (of a particle) and a second layer of ions and water held to the first layer by attractive force. The thickness of both fixed layer and second layer depend on the charge on the particle and type of ions in
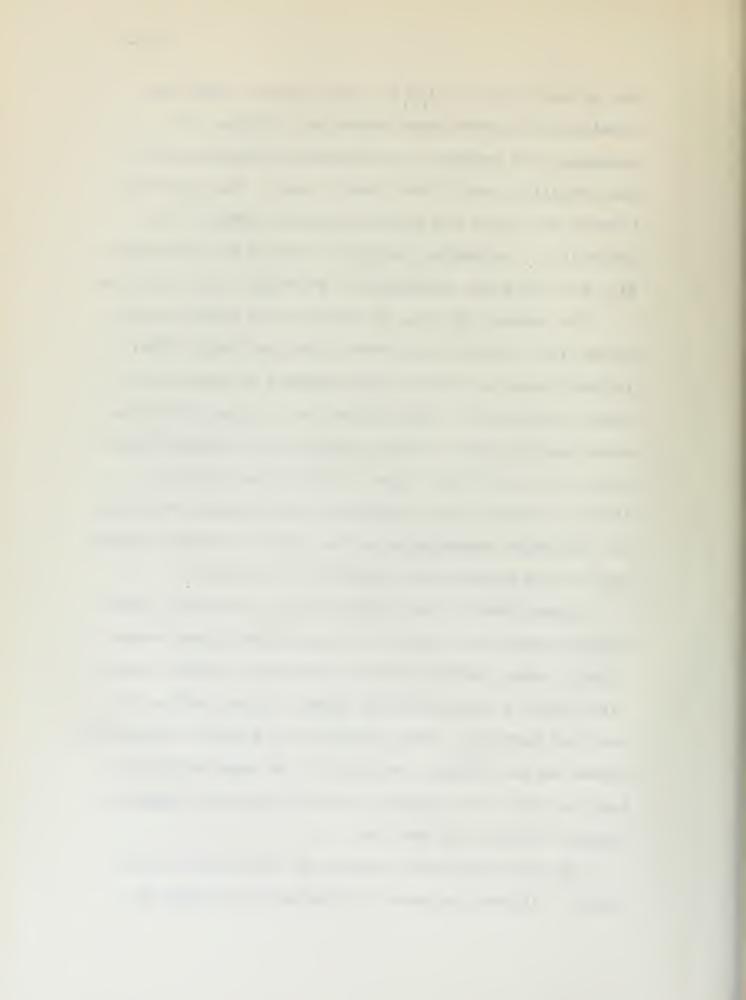
the second layer as will be noted later. Helmholtz
considered this two layer structural similar to a
condenser and obtained a mathematical expression for
the potential across this double layer. The potential
between the fixed and second layers he termed "zeta
potential". Helmholtz' original concept has been modi-
fied but the basic mathematical principle still applies.

The current theory, as developed by many investi-
gators (see Overbeek and Verwey 1948 and Kruyt 1949)
is that there is a thin layer composed of water mole-
cules, considered a fixed layer, and a layer of diffuse
water molecules and cations, which is of varying thick-
ness, above the fixed layer. This second layer of
diffuse ions and water molecules is of varying rigidity
and thickness depending upon the size of particle charge,
type of ion present and amount of ion present.

Jenny (1936), Gouy (1910), Debye and Huckel (1923)
have developed and used this concept with minor varia-
tions. Jenny (1936) considered that the cations oscil-
lated about a negative point charge on the surface of
the clay particle. This concept of a kinetic oscillation
volume in the diffuse ion layer is an important one to
bear in mind and a logical one based upon the inherent
thermal activity of the ion.

The zeta potential between the fixed water layer
and the diffuse ion layer is discussed at length by

Preece (1947), Lambe (1953b), and fully covered by Overbeck and Verwey (1948) and Kruyt (1949) from a colloidal standpoint. Preece and Lambe developed their articles based upon Overbeck, Verwey and Kruyt.

The characteristics of zeta potential which will affect most considerations of the influence of ions on engineering properties of soils are the "streaming potential" and ion concentration effect on zeta potential.

Considering in sequence from the surface of a particle outward, we have a fixed water layer, a partially immobilized water layer with diffuse ions presenting a viscous layer, and finally free water. The "streaming potential" may be considered simply as the potential due to frictional drag of the free water on the diffuse layer, due to the resistance of the diffuse layer to flow, when a pressure or head is applied to the free water. The tendency of the free water movement to move the diffuse layer in relation to the particle is resisted by the zeta potential between the particle fixed layer and diffuse layer and tends to reduce the zeta potential.

The greater the concentration of ions in the diffuse layer, the less the zeta potential. Also, for an equivalent concentration of monovalent ions and divalent or polyvalent ions, the zeta potential is less for the polyvalent ions. Simply, the higher the valence of the adsorbed cation the less the zeta potential is.

Also the greater the ion concentration the less the
zeta potential.

These characteristics of zeta potential will be
considered in explanation of certain phenomena discussed
later.

Up to now we have not considered the structure
of the "fixed" layer of water molecules attached to
the particle surface or the structure of the diffuse
layer. It is considered that this structure may be
of the utmost importance in understanding ionic
phenomena.

Banos and Winterkorn (1936) and Winterkorn (1943)
have presented evidence that the fixed water film
attached to clay particles actually exists. Russell
(1938) (Grim 1953) points out that structural character-
istics of soil require a non liquid fixed film of
initially adsorbed water. Forslind (1958) (Grim 1953)
has reported electron diffraction data which seems to
indicate a water structure in the fixed layer on mont-
morillonite similar to ice. Macey (1942) arguing from
the similarity between the structure of ice and oxygen
atoms in the clay particle surface has postulated that
the initially adsorbed water has the structure of ice.

The characteristics of water molecules themselves
give evidence of the possibility of grouping into a
structure of some type on the surface of clay. Several

investigators (Grim 1953) have postulated that by the
"dipole" nature of the water molecules, and the bonding
of the hydrogens to form linkages between water molecules,
that the water molecules would attach themselves to the
O ions in the surface of the mineral lattice through
an H bond. Since the oxygen ions in the crystal sur-
face have a definite configuration the bonded water would
have a definite configuration or structure also.
Hendricks and Jefferson (1938), Barshad (1949), Mering
(1946), Hendricks, Nelson and Alexander (1940) (all
after Grim 1953) all postulate some type of structure
to the "fixed" water film layer. Until additional
confirmative evidence is presented the exact nature
of the fixed water layer will be in doubt. It appears
obvious however that there is a definite structure
to the fixed layer adsorbed water molecules. This con-
cept is of extreme importance in furthering an under-
standing of the soil. There is some disagreement as
to whether the structure consists of closely packed
water molecules or an open network. The predominance
of opinion seems to favor an open structural network.

Assuming a definite structural configuration of
water molecules in the fixed water layer we may now
inquire regarding the thickness of the layer. Due to
the kinetic energy of the water molecules the adsorbed
fixed water layer could be expected to extend from the

clay particle surface only a short distance. Numerous
investigators have attempted to estimate this water
film thickness without too close agreement. The general
range of values estimated however is indicative of the
probable thickness. The values range from 7.5 A. to
25 A. and probably vary considerably depending upon
the clay mineral. This is discussed by Grim (1953).
Various investigators suggest that evidence indicates
a transition from the fixed layer to the second ion
swarm layer of varying degrees. This transition appears
to depend upon the type of adsorbed ion in the second
layer. Grim and Cuthbert (1945) conclude that for
the Ca ion on montmorillonite the transition is abrupt
while for the Na ion the transition is gradual. With
Na the water above the fixed layer may be oriented and
partially immobilized for 100 or more angstroms beyond
the particle surface.

Winterkorn (1943) concludes that water held directly
on clay-mineral surfaces must be considered fixed (solid)
and that the change of state of water from the fixed
layer to free water is a gradual change which varies
exponentially, with distance of the water from the
clay surface.

Considering the second layer of water on the clay
particle we have just noted that the water molecules
in this layer may be oriented to varying degrees outward

from the fixed layer. The thickness of this layer of
water molecules and adsorbed ions will vary depending
once again upon the type of clay particle, and type of
adsorbed ion. The concentration of ions in this layer
will vary with distance from the clay particle surface
and gradually decrease until the thermal activity of the
ions overcomes any tendency for concentration. The
effect of ions on clay-water relationships will be
briefly discussed later under ion phenomena.

Other concepts of ion exchange and adsorption have
been proposed. The most noteworthy of these is the
series of papers by Mattson from 1929 to 1941. Mattson
considers the soil to consist of "acidoids" such as
silicic acid and H ions and "basoids" such as aluminum
and iron hydroxides. Explanation of ionic phenomena
are based on the relationships of "acidoid" to "basoid".
Mattson changed his views somewhat over the years but
did not finally present any substantiated "laws".
Most of his work is theoretical and not backed by
experimental data. It is considered that the investi-
gator of ionic phenomena should be familiar with this
work because it does present some interesting points
and is often used and referred to by soil scientists.
Kelley (1943) presents and informative critical review of
Mattsons work.

For many years soil scientists have attempted to

formulate equations which would show a soluable relation-
ship between the adsorbed ions, concentration of ions,
type of ion and type of clay.

These equations, called equilibrium formulas, have
been based upon the law of mass action, thermodynamic
consideration, thermochemical consideration, Donnan
equilibrium, "acidoid-basoid" consideration and varia-
tions of these. Guggenheim (1944), Vanselow (1932),
Gapon (1933) Johnson (1941), Marshall and Gupta (1933)
and others have presented formulas. These formulas
have been checked experimentally, reviewed, and dis-
cussed by Davis (1945), Melstead and Bray (1947),
Melsted (1943), Coleman (1952), Marshall and Gupta
(1933), Kelley (1948), Boorland and Reitemeier (1950),
Magistad (1944), Eriksson (1952), Davis (1942), and
Krishnamoorthy and Overstreet (1948, 1949, 1950 a,
1950 b) and others.

The general opinion of the various investigators
is that many of the equations are variations of the
same idea, that theoretically they are sound, but are
not fully applicable. The determination of constants
in the equation is not readily possible. The formulas,
in general, can be applied to a closed equilibrium system
of one soil and one cation but because of the indeter-
minate nature of the factors required cannot be generally
applied.

These equilibrium equations are not to be completely discarded for application in understanding the engineering properties of complex soil masses for they are in general theoretically sound. An understanding of their theory is essential to help in understanding the basic science of soil-water-ion relationships. A detailed presentation of these equations and theory is beyond the time scope of this paper, in fact, could be the subject of a separate paper.

In summary it is the author's opinion that the theory which best applies to investigations and explanations of ion effect on engineering properties of soil is the modified double layer theory. This theory is not at variance with the basic science behind other theories but is a developed concept more applicable to our engineering field. For clarity this concept is again briefly reviewed.

The clay particles, primarily responsible for ion adsorption in a soil complex, are crystalline minerals with a predominately negative charge. This negative charge is the seat of attraction for positive cations in the soil. The structure of the clay and ion relationship is considered a double layer on the clay particle surface. The first layer on the surface is a fixed layer of water molecules attached to the surface by a hydrogen bond. This fixed layer has a definite

structure dictated by the clay mineral, water molecule
action, and adsorbed ion. The second layer is of varying
thickness and water molecule orientation depending
upon the ion present and clay mineral. This second
layer contains adsorbed ions. In addition it is pro-
posed that adsorbed ions may be present in structural
spaces of the fixed layer. The kinetic aspect of the
second layer should also be borne in mind. Jenny's
concept of an "oscillation volume" has been mentioned.
The normal thermal activity of the ions would preclude
them being held in a fixed position. Jenny (1939)
demonstrated that the ions migrate from particle to
particle. Borland and Reitemeir established by radio-
active Ca that the adsorbed ions were in equilibrium
with the same ion in the free water solution and that
an interchange took place from adsorbed layer to free
water and vice versa. Other investigators have shown
the migration of ions from particle to particle to be
accomplished in preference to migration through the
free water exchange.

The anion exchange mechanism in soil must also
be briefly discussed. Many investigators (Grim 1953)
have shown that clay minerals exhibit anion exchange
capacity. Investigation of anion exchange has been
difficult because it may involve a breakdown of the
original mineral. Fortunately many investigators have

shown that anions have only a small effect upon cation exchange capacity which is large enough to be the domination factor in soils. Briefly, anion exchange may occur through replacement of OH ions on the broken bond edges of mineral sheets, it may occur through attraction of positive valence ions in the broken bond edge as noted by Thiessen. The OH replacement has been demonstrated (Grim 1953). Replacement of OH may occur to some extent not only on edges but on the surface of the lattice sheet, particularly in montmorillonite. Dean and Rubin (1947) have shown that anion exchange varies directly as the surface area of the clay mineral which tends toward the OH replacement concept.

ION EXCHANGE - ION PHENOMENA

The proper manner in which to start a discussion of the adsorption phenomena of specific ions on clay particles is to state that there are contradictions at every point and that no experimental results are really conclusive. This may sound discouraging but eventually through a more clear understanding of soil science as a whole a definite pattern may be formed. For the present we can only indicate trends with the reservation that all trends have exceptions.

A detailed discussion of specific ion adsorption, and factors affecting variations in specific ion adsorption, is contained in Grim (1953), Kelley (1948), Baver (1948) Marshall (1944) and Lutz and Chandler (1946). The complexity of factors precludes a detailed presentation in this paper and only a few general trends will be noted.

It should be pointed out that apparent contradictions in ionic phenomena experimental results is in part due to the lack of proper technique and failure to realize the presence of factors involved which may cloud the final results and cause misinterpretation. As an example, many investigators use the technique of electrodialysis for removal of exchangeable ions. Electrodialysis consists of passing an electric current through a suspension of the mineral being investigated

in a special cell thus driving off the exchangeable
ions. Many investigators have given conclusive evidence
(Grim 1953) that electrodialysis will not completely
remove exchangeable ions without causing a partial
breakdown of the clay mineral due to stripping off
lattice surface ions. This, of course, changes the
characteristic of the mineral so that adsorption of
subsequent ions is not comparable between samples be-
cause of varying degrees of breakdown and removal of
surface ions affecting the adsorption of a particular
ion. This technique of electrodialysis has been used
by the greater percentage of investigators in preparing
samples saturated with one ion.

Other techniques to remove exchangeable ions and
saturate a sample with other ions have similar defects.
Various investigators have shown that the type of salt
used to saturate the clay with ions changes the amount
of ion adsorption. This is in part due to anion masking
effect and in part to surface structural changes. Prior
to saturating a sample with a particular ion, most in-
vestigators remove all existing ions by saturating with
the H ion. This is frequently carried out by using
A .05 N solution of H Cl as an alternate to electro-
dialysis. In saturating with H the acid again attacks
the soil mineral structure and it has been found that
Al is removed from the lattice and placed in an ex-

exchangeable position and that the edges are more sus-
ceptible to breakdown of silica by subsequent use or
formation of alkaline solutions. Frequently, therefore,
when an investigator believes he has a single ion in
replaceable positions he actually may have an appreciable
amount of Al which may mask effects of the other ion.

Another primary difficulty in determining the
relative activity of ions is in the actual technique
of measuring the base exchange capacity. The pH of
the sample, the type and relative percent of clay in
the sample and the type of ion present all cause varia-
tion in capacity. A rigidly controlled technique must
be used throughout to obtain comparable exchange capacity
values.

That some soil scientists recognize the various
shortcomings in investigative technique is indicated
in current literature where new techniques are being
explored and old techniques revised.

An important consideration in evaluating ion data
experiments is the concentration of the ion salt being
used. It has been shown that the effect of concentra-
tion of the replacing ion depends upon the kind of cation
being replaced and the relative valence of the two
cations. Ions of the same valence are little affected
by change in concentration. Ions of different valence
show marked changes in the amount of ion replaced.

Increasing concentration for different valence ions usually results in increased amounts exchanged.

The relative replacing power of ions of the same concentration varies with the type of mineral. Jenny (1932) proposed that the order of replacement of ions was directly related to the hydration of the ion. A reversal of the series of Jenny for each clay mineral was found by other investigators (Grim 1953) to take place when an alcohol medium was used instead of water. Hendricks, Nelson, and Alexander (1940) have presented evidence that the Na, H, and K ions are not hydrated when absorbed and that Ca and Li are only partially hydrated. Other investigators (Grim 1953) have suggest- ted that the order of replacement is related to the polarization of the ion which is determined by valence and ion size. The more highly polarized the ion is, the more difficult it is to replace. The polarization increases with increased valence and decreased ion size. This approach is rational in view of the adsorption forces involved but once again does not explain fully the action of all ions. It is partially corroborated by the general rule that the polyvalent ions are more strongly adsorbed and held than the monovalent ions.

The lyotropic series of adsorption and replacement of ions was proposed by Jenny (1932). This series is based in general upon the hydrated ion size. The

smaller the crystal ion, the more highly hydrated and
the weaker it is in ionic adsorption. The H ion, which
is the most strongly adsorbed and held ion, does not
conform readily to this theory. Jenny proposed that
the H ion entered into a chemical combination with OH
and O ions in the mineral surface. The recent work
(Grim 1953) which tends to indicate the H ion is un-
hydrated may be a better explanation. Another suggestion
is that the H ion may combine with the fixed water
molecules in a strong combination. The confirmation
by physical chemists of the quantity of H_3O in water
suggests a relationship of this type with the fixed
water molecules may be possible.

The K ion is also out of place in the lyotropic
series in the replaceability series. K is not released
as readily. The most logical explanation for this
appears to be the assumption that some K is partially
immobilized on the surface and between the basal planes
of the particles. The size of the K ion would permit
it to fit in the depressions of the surface sheets.
This is further borne out by the "fixation" of K in
montmorillonite upon drying the sample. The K becomes
irreplaceable due to its position and increased bonding
energy upon removal of water molecules. Once again,
however, (Grim 1953) many investigators have shown the
variation in fixation of K due to different minerals

and the presence of other adsorbed ions. The ammonia
ion has been found to behave in a manner similar to K.

The effect of mineral type on K adsorption and
fixation has been investigated by Levine and Joffe
(1947), Barber and Marshall (1952) and others. In
general layer minerals such as illites and montmorillo-
nites will retain a certain amount of adsorbed K.
Montmorillonites will retain more than illites since
some K is already fixed between illite layers. Kaolin
will not fix K in any appreciable amount. The smaller
the particle the faster K is adsorbed in layer minerals.
The greater the replacement of Fe and Al for Si in the
mineral the more K adsorbed and fixed in irreplaceable
position.

Other factors influencing the type and amount of
ion adsorbed and the energy of adsorption are the pre-
sence of other ions. Most natural soils contain a
mixture of two to ten different ions adsorbed on the
soil particles. Many investigators have determined
the effect of the presence of one ion on one other ion
on a particular soil. Minor variations in the lyotro-
pic series of Jenny have been determined, depending upon
the ions present, the ion being adsorbed and the type
of mineral. The effect of anions has also been studied
and in general they reduce a negligible amount the
quantity of cations adsorbed and cause minor variations

in the lyotropic series.

The presence of two particular free ions in a soil mass cause a great deal of erratic behavior in ion adsorption. These ions are Al and Fe. The size of these ions and their high valence may result in their masking attraction for other ions from inside the particle. These ions have been found by many investigators to "coat" the soil particles excluding other ions. A second effect is the formation of free oxides and hydroxides which may produce a gel which has ion adsorptive powers of its own thus "stealing" ions from the other particles. Fe also seriously affects mineral X-Ray analysis by clouding spectra lines. The removal of Fe is particularly difficult also since techniques, usually acid, for removal also cause mineral breakdown.

Another seriously disturbing factor in investigation and determination of ionic phenomena is the effect of organic matter. Baver (1930) and others have determined that organic matter in general, increases the ion exchange capacity of the soil mass. Certain organic complex ions form soluble salts with monovalent cations and insoluble salts with divalent cations (Norman and Bartholomew 1943). Other organic decomposition products form adsorptive gel like complexes which remove ions from the soil water. Many organic cations react like inorganic cations and are adsorbed by the clay

particles. This has an effect upon the adsorption of inorganic ions since the organic cations are usually very large and "mask" more than one exchange position on the particle. The subject of organic ions is covered extensively in Grim 1953.

In retrospect we can state that, in general, the lyotropic series of Jenny will indicate the general energy with which ions are held and adsorbed, subject to variations in actual soils due to factors noted. The "hydration" theory is probably not the explanation for this series.

It is the belief of the author that ionic phenomena are directly related to the double layer water structure proposed under the Ionic Theory section. A careful study of known phenomena related to ion size and the size of openings in the water structure of the "fixed" water layer may indicate a possible explanation for many of these phenomena. The variation of the H ion, unhydrated, would be an example. Due to its small size it can readily pass through the openings in the fixed water structure entering into a higher energy bond on the particle surface. The action of the K and Na ions would also fit this theory. This theory would not be "blanket" in its coverage but would have to consider the clay mineral and ion energy also. Such an investigation is beyond the scope of this paper and may be

considered a separate subject of investigation.

In closing this section, mention must be made of one other factor influencing ionic reactions. Waksman (1927), Winterkorn (1948), Roberts (1947), Allison and Scarseth (1942), Hurwitz and Batchelor (1943) and Starkey and Halvorson (1927) all show that soil bacteria have an effect upon the soil ions. Hurwitz and Batchelor indicate that micro-organisms in the soil make K non-exchangeable by adsorbing it themselves. Roberts, Allison and Scarseth and others show that bacteria in the soil will reduce appreciable amounts of ferric iron present to ferrous iron of lower valence. Other bacteria sorb Ca and use it. Bacteria also have a great effect in the production of organic ions by decomposing organic matter. The entire subject of the effect of soil bacteria on ions requires much investigation. That the importance of this is recognized is shown in recent literature.

ION EFFECTS ON THE ENGINEERING
PROPERTIES OF SOIL

The earliest concrete recognition of the possibility
that ions may affect the engineering properties of soils is
that of Winterkorn (1936). In 1940, Winterkorn, and separa-
tely Rapp, presented additional experimental data on some
effects of ions on certain soil engineering properties.
Since that time, the subject has been increasingly recog-
nized in engineering literature, but is obviously still not
very well understood or appreciated by most engineers. This
is noted from the failure to appreciate its significance in
asphalt, cement, and calcium chloride soil stabilization by
most people in those fields. Those who do recognize that
there are ionic relationships do not know enough about them
to investigate more fully. In the large amount of literature
on calcium chloride soil stabilization, much work has been
done on the effect of varying percentages of calcium chloride
on soil properties, but the soil constituents, water content,
and other pertinent factors have never been investigated in
conjunction with this work. Much of the data is meaningless
except for application to a particular soil tested.

The ultimate goal of the effect of ions on soil proper-
ties is, of course, control of the properties of a soil as
applicable to the particular engineering application being
considered. Currently, the investigations into control of
engineering properties may be roughly lumped into three

categories. First, control by chemical additions in which
the chemicals enter into energy relationships of an ionic
nature with the soil particles. Calcium chloride, asphalt,
soil cement, and certain organic compounds enter into this
category. Second, electro-osmotic control of soil strength,
both permanently, by adding ionic compounds, and temporarily,
by electrical current flow only. Third, control by chemical
additions to the soil which enter into a purely "mechanical"
bonding relationship with soil particles. Organic polymers,
sulphite liquor and sodium silicate are of this nature.

Murray (1952) presents a good brief summary of mainly
chemical-mechanical means. Michaels (1952) presents a con-
cise summary which covers well the physico-chemical approach
through ion relationships. Koonce (1954) presents an
excellent summary of the electro-osmotic field.

In investigating the literature concerning the effect
of ions on soil engineering properties, there appears to be
a relationship between the type of ion and its effect upon
the particle water films. Winterkorn (1942, 1948b), Grim and
Cuthbert (1945 a and b), Grim (1948), Salas and Serratosa
(1953), Winterkorn and Bauer (1934), Winterkorn and Eckert
(1940), Lambe (1953), Michaels (1952), Johnson and Davidson
(1947), and others have all emphasized this point. The exact
nature of the effect of ions upon water-soil particle relat-
ionship is not clearly defined. Different investigators

have suggested various possibilities, but most seem to agree
that the variation in thickness of the adsorbed water layer,
above the fixed water layer on the soil particle, is the
reason for the change in engineering properties with change
in adsorbed ion. The manner in which the adsorbed ion accom-
plishes the change in thickness of the water layer is not
understood, and data is lacking to develop this understanding,
as previously noted under ionic theory and effects. Preece
(1947), Salas and Serratosa (1953), Lambe (1953), Chu and
Davidson (1952), andothers specifically attribute the change
in thickness of adsorbed water to be due to a change in zeta
potential occasioned by the ion. This conclusion is logical
and in accord with previously noted theory. Winterkorn does
not prefer a specific explanation, but states the ion effect
on the water films is a mechanism about which not enough is
known to postulate the exact operation. Grim recognizes the
effect, but like Winterkorn, will not postulate a definite
relationship. Many investigators prefer the "hydrated ion"
theory on the basis that the water of hydration of the ion
varies the adsorbed water layer thickness. As will be noted,
some data tends to bear this out in that certain properties
roughly follow Jenny's lyotropic series. Previously noted,
however, is the doubt as to the hydration of ions. After
presentation of various data as to the specific effects of
ions on soil properties, the subject of mechanism of effect
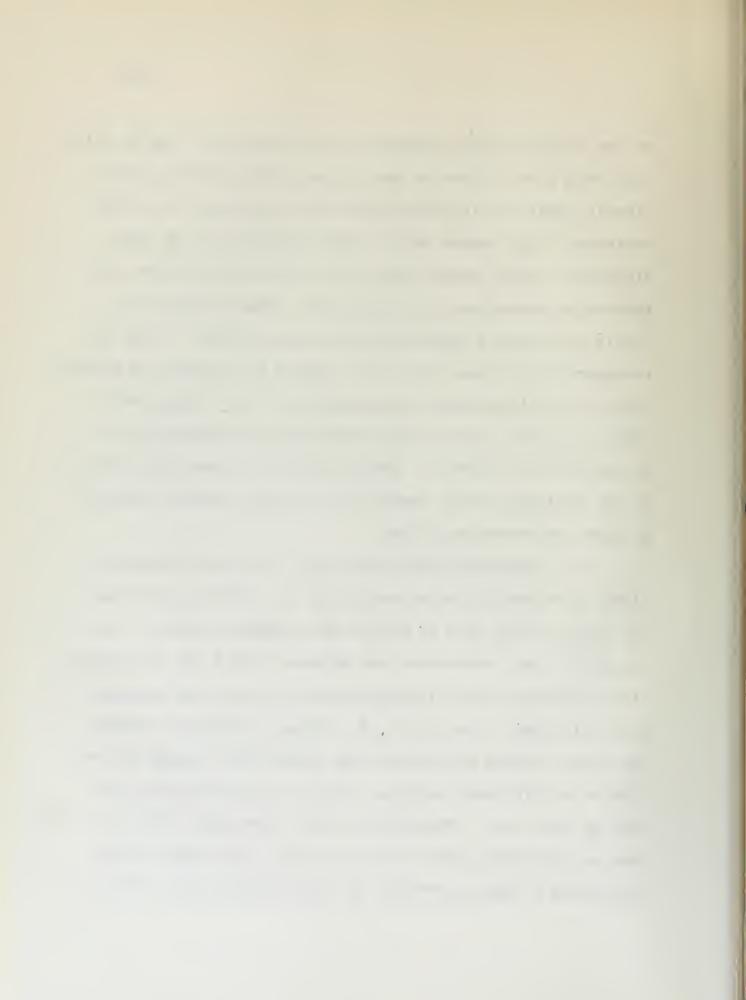
will be summarized.

The logical manner in which to consider ions and soil properties is under each of the soil properties individually.

A property of soils familiar to all engineers is plasticity as determined by the Atterberg limits. The limits consist, for engineering purposes, of the liquid limit, the plastic limit, and the plastic index. The shrinkage limit is used in this category also. The liquid limit is defined as that maximum water content at which the soil first exhibits a small, but measurable shear resistance. The plastic limit is the water content at which the soil will crumble rather than distort plastically upon decreasing water content from the liquid limit. The range of water content between the plastic limit and liquid limit is a relative measure of plastic behavior of the soil, called the plastic index. The shrinkage limit is that water content where a further decrease in water will not cause a change in void volume or shrinkage of the sample.

The Atterberg limits were originally developed and used by the ceramics industry. Russel and Wehr (1928) determined that organic content varied the liquid limit and plastic index of soils. This is mentioned since adsorbed organic ions may have contributed in part to the changes. Endell, Loos and Breth (1939) determined that Na increases the liquid limit of a quartz-montmorillonite soil, but had little effect

on the plastic limit compared to a Ca ion soil. The Na soil
also held 3 to 4 times as much water as the Ca soil. The
plastic index was increased about four times for Na. The
shrinkage limit showed only a small increase for Na soil.
Winterkorn (1936) showed that for a Na-montmorillonite soil
increasing concentration of Na in the sample reduced the
liquid and plastic limits and the plastic index. K and Ca
treatment of the same soil also reduced the liquid and plastic
limits with increasing concentration of ion. The plastic
index increased slightly with increasing concentration of
Ca and decreased with K. There was not an appreciable effect
on the shrinkage limit except for a notable sudden increase
at high concentration of Na.

For a montmorillonite type soil, Salas and Serratosa
(1953) give the following series of the effect on raising
the liquid limit with Li having the greatest effect: Li,
Na, K, Ca, Ba. Winterkorn and Moorman (1941) and Winterkorn
(1942) indicate the following series for the same increase
in liquid limit: Na, Ca, H, K. Holmes, Roediger, Wirsig
and Snyder (1943) do not find any appreciable change in any
limits for different cations. This is believed due to the
type of soil used. Winterkorn (1942) shows the effect of
ions on Atterberg limits for four soils. For three soils
containing a high percentage of clay fraction, the effect

was approximately as noted above: Na, Ca, H, Al, Fe, Mg, K, in decreasing order of effect. One soil low in clay fraction had the order H, K, Na, Ca. Ennis and Huff (1951) have indicated an increase in plastic index and in liquid limit for kaolinite and illite. Grim (1948) indicates an increase in liquid limit and plastic index for montmorillonite, and a very slight increase for kaolin and illite.
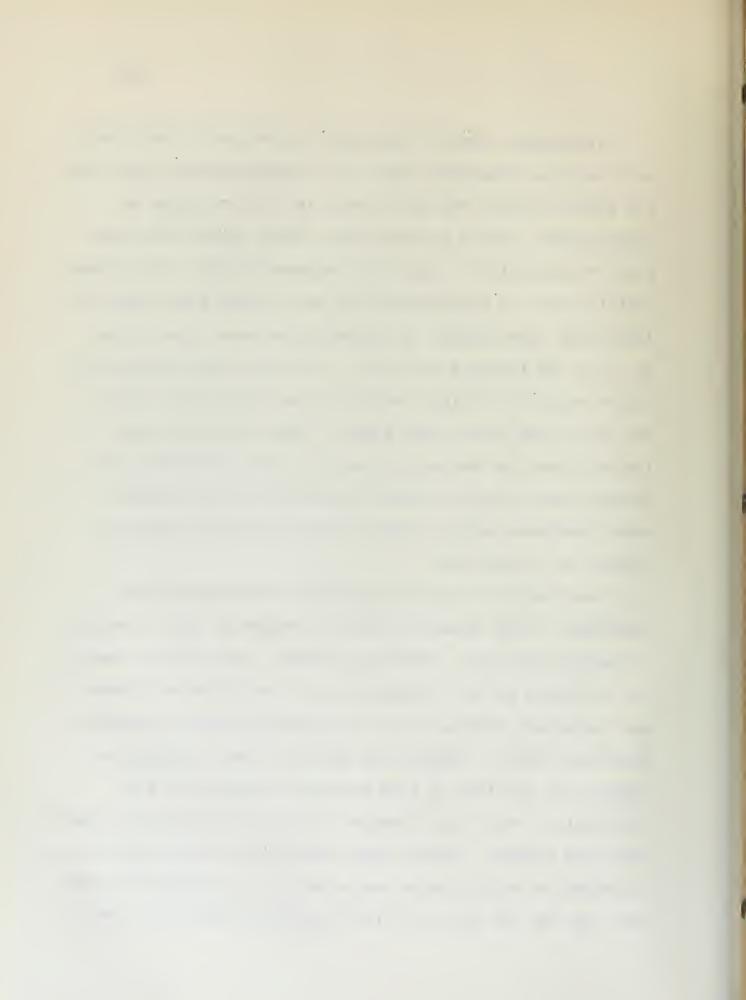
In summary, we can say that ions affect the liquid limit and plastic index by increasing them, but have little effect on the plastic limit or shrinkage limit. In general, on the clay fraction of a soil, the degree of effect is approximately in order of the lyotropic series of Jenny. Montmorillonites, which have a large water adsorptive capacity on interplanor spaces, are affected the most. Kaolinite and illite are affected only to a small degree. The degree of ion effect is directly proportional to the base exchange capacity of the soil and clay content.

It has been noted by several agricultural soil scientists that adsorbed ions increase the specific gravity of the soil. Winterkorn (1942) indicated that the specific gravity was affected in the following order of adsorbed ions: Na, Ca, H, Fe, K, Mg., for a montmorillonite type soil with Na giving the highest specific gravity. Again we have an indication that the thickness of the adsorbed water follows a rough series similar to the lyotropic.

Winterkorn (1940b), Winterkorn and Moorman (1941) indicate that the adsorptive power of a montmorillonite type soil for water followed the same series as for the change in liquid limit. Salas and Serratosa (1953) checked the time rate of adsorption of water in a montmorillonite. They found that the rate of adsorption of Ba and Ca soil soon levels off, increasing very slowly. K adsorbed more water than either Ba or Ca and levelled off also. Li and Na soil continued to adsorb water at a fairly constantly increasing rate until the end of the test at 220 hours. This difference would indicate that the Na and Li ions are slowly adsorbed, and hydrate more slowly, or that orientation of the adsorbed water continues out to a great distance from the particle surface at a slow rate.

Swelling of a soil is associated primarily with the expanding lattice minerals, and is apparently also a function of the adsorbed ion. Winterkorn (1936) indicated that swelling decreased as the concentration of ion in the soil water was increased, similar to ion concentration effect upon the Atterberg limits. Johnson and Davidson (1947) indicate an increase in swelling of a Na kaolinite compared to a Ca kaolinite. These would compare to water adsorption for the same type mineral. Bower (1948) indicates the swelling varies according to the following series with Li producing the greatest: Li, Na, Ca, Ba, H, K, for a montmorillonite type soil.
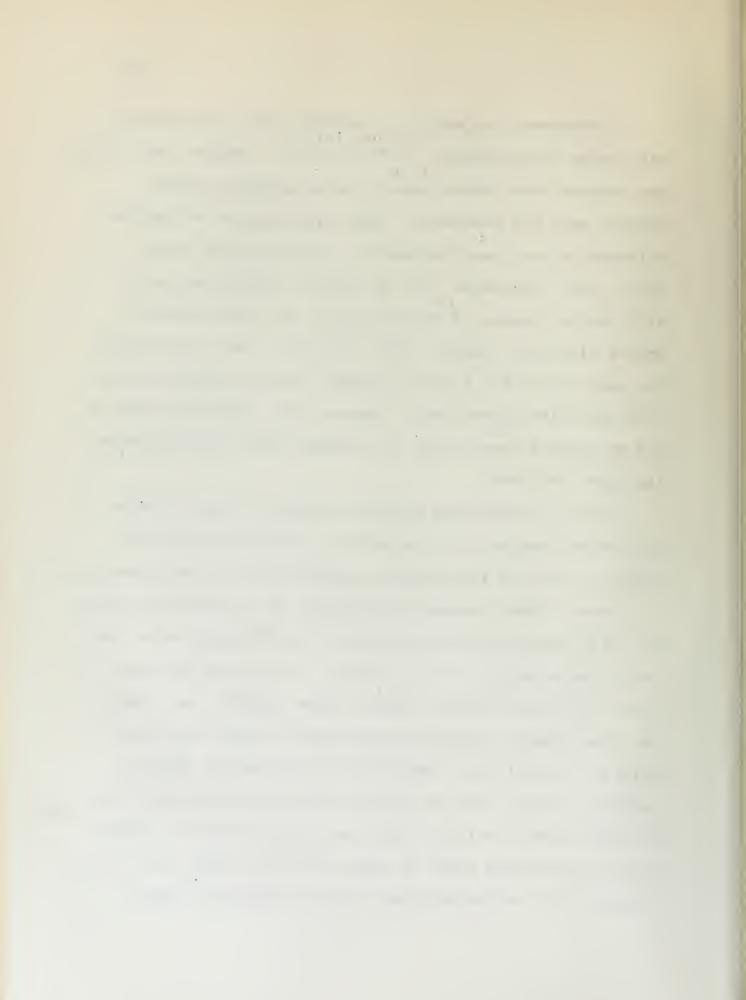
A phenomena due mainly to particle size, but involved with water relationships, is frost heave. Beskow (1947 a & b) has reduced frost heave rate by using alkaline resins. Details were not available. Many investigators of calcium chloride effects have indicated it reduces frost heave. Slate (1942) indicates that 2% calcium chloride protects silt against heave, 1% protects clay, and 1/2% protects graded mixtures. Endell (1941) indicates that a Ca-bentonite quartz soil had a rate of heave 1 mm./hr. greater than a Na-bentonite quartz soil. Preece (1947) indicates both Ca and Na reduced frost heave of a natural soil, with Na reducing heave the most.

Prior to describing further effects of ions on water soil relationships, it is necessary to briefly note the effect of ions on flocculation and dispersion of soil particles.

Baver (1948) presents an analysis of flocculation being due to a change in zeta potential of the adsorbed water and change in potential of the particle. Salas and Serratosa (1953), Chu and Davidson (1952), Lambe (1953b), and others use this concept (originally the work of Jenny and Reitemeier). To avoid the complicated relationships between particle charge, type of ion on particle and replacing ion, we shall simply indicate that flocculation power of common ions in decreasing order of power are H, Ca, Mg, K, Na. The effect of the anions with the various cations is large.

Briefly, the phosphate and polyphosphate salts of Na are the best dispersants. Michaels (1952), Wintermeyer (1953), Winterkorn (1936), and others all present data on flocculation and dispersion. Puri and Rai (1944) determined that a Na soil gave a fine crumb structure which was not destroyed by water. Ruehrwein and Ward (1952) indicate that an organic polycation from Na polymethacrylate was an effective flocculant. In this case, flocculation was by the Na being attached to the particles and the polymer forming long chain molecule bridges between. The recent development of "Krilium", a complex organic polvelectrolyte, indicates that the organic ion field may prove fruitful.

The effect of ions on permeability is a complex mechanism involving a combination of ion effect on water layer thickness and flocculation, or dispersion of fine soil particles. Winterkorn and Moorman (1941) present inconclusive data on ions and permeability.

The effect of ions upon the soil structure is a subject for a separate paper due to the factors involved. It concerns the soil during its formation, effects of ground water containing ions, and is involved with flocculation also. Lambe (1953) presents a brief outline of effects based upon change in potentials.

Winterkorn and Moorman (1941) indicate an increase from a friction angle of 12 degrees for a Na soil to 22 degrees

for K soil. This is based upon the thinner water films and
tighter flocculent structure for K than Na.

Cohesion in a clay soil, which is most active with ions,
is directly related to shear resistance. Grim and Cuthbert
(1945a) indicate that maximum cohesion would occur when the
clay adsorbed water has a maximum thickness and rigidity for
a given clay content, and cohesion will be reduced if water
thickness is greater or less than this critical value.
Winterkorn and Moorman (1941), from direct shear tests,
indicate K gives a higher shear strength than Na. This would
conform to the water film theory of Grim and Cuthbert.
Sullivan (1939) made a detailed analysis of ion effect on
shear using a ceramic industry torque machine. He found the
following series in order of increasing maximum torque: Li,
Na, Ca, Ba, Mg, Al, Fe, K, H, NH_4. This series, except for
ammonia, follows known properties of these ions as to floc-
culating and water orientation characteristics. The order
of increasing yield point followed the same series. The
order of increasing angle at maximum torque was Fe, H, Al,
NH_4, Ca, K, Mg, Ba, Na, and Li. It was of interest that the
properties of shear resistance were reduced when the clay was
saturated with ions on the natural soil sample, compared to
saturating first with H, then with the ion. This could be
attributed to incomplete replacement on the natural soil.

Winterkorn and Moorman (1941), Preece (1947), Salas and Serratosa (1953), Lambe (1953b), Winterkorn (1936) all present data on the compressibility of clays and clay soils. In general, Na soils have a lower speed of compression, but greater total consolidation. The ions again affect consolidation on the basis of water layer thickness plus, in ions other than Na, complex relationships of energy of attraction and repulsion of particles affecting permeability. Roughly, due to higher void ratio to start, the order of amount of consolidation is in the decreasing order: Li, Na, Ca, K, Ba. Salas and Serratosa (1953) and Lambe (1953b) report on consolidation using organic liquids. This data was not conclusive. It was interesting to note that at higher pressures of consolidation, the effect of ions is less pronounced. It is suggested that high pressure consolidation tests may be an indicia of the effect and magnitude of ions on total consolidation.

The important property of compaction and ions has been studied by Yoder (1947), Johnson (1946), Winterkorn (1940a and 1942), Winterkorn and Moorman (1941). Once again, it is noted that the effect of ions on adsorbed water layers produce differences. In general, those ions which produce the thicker water layers and orient water better, produce the greatest density at lower water content. For a given water content, less compactive effort was required for the better

water orienting ions to produce a given density. Na and Ca both produce this effect among common ions used with Na producing the greatest density for a given water content and compaction effort.

The chemical stabilization of soil has long been a subject of research, much of it uncoordinated. Under this heading, we can consider soil-cement and asphalt stabilization.

Catton (1940), from his research into soil cement ratios, concluded that his results indicated a factor in the soil, not determined, which improved soil-cement ratios in certain soils by lowering required per cent of cement for equivalent hardening of soil. He attributed the affinity of certain soils for cement to possible ion effects. In this he was correct, for detailed investigation by Winterkorn (1942) in ions and soil-cement ratios, determined that certain ions improved the "hardening" (strength) of soil by cement, considerably. There was no definite inclusive series, but the effect varied with the type of soil with K, Na, Ca, H, and Al giving the greatest effect.

Winterkorn (1940a) determined that ions present greatly affect the retention and wase of stabilization of soil with bitumen. In general, the greater the ion valence and the higher the base exchange capacity of the soil, the better the stabilization. Holmes, Roediger, Wirsig and Snyder (1943) also determined ions affect asphalt stabilization. Winterkorn

(1940b) again notes the effect of ions on asphalt stabilization.

Slesser (1943) and Slate (1940) determined that calcium chloride, applied for soil stabilization, migrates downward and laterally. It was also determined that sodium chloride tends to be carried upward and crystallizes on the surface. When chemical stabilization is better understood and controlled, the leaching out of applied chemical and its migration, will be important.

Physico-chemical stabilization using organic compounds has been investigated more thoroughly recently. Lambe (1951, 1953a) presents results showing increased soil strength using Ca and Na acrylates which are polymerized. He proposes that the Na and Ca ions are adsorbed on the soil and then attached to the complex organic polymer which acts as a chain to tie particles together.

Smith (1952) reports the results of use of chrome-sulphite liquor, which is a waste product, on stabilization. Results are that it is more effective on clays, perhaps due to ion bond than on coarse material. It leaches out of soil readily.

Riedel (1952) and Keil (1953) report on mechanical-chemical means of stabilization by formation of silica gels.

Organic chemicals have been used to stabilize soil by "waterproofing" soil particles. Maclean and Clare (1953) report good results with organic resins. Grim (1948, 1953) reports the possible effect of organic cations being adsorbed to the exclusion of water. Beskow (1947) also reports on organic resins being satisfactory to reduce water intake.

A difficulty with the use of organic chemicals which is now receiving some attention is the destruction and changing of organic compounds by soil bacteria. Winterkorn (1948a), Jones (1948), Eustis (1948), Waksman (1927), and Tschebotarioff and Winterkorn (1947) all report the detrimental effect of bacteria upon organic soil stabilizers. Recommendations for the use of germicides to be included with organic compounds are made by Winterkorn (1948) and Jones (1948).

The subject of thixotropy in soils is of much interest to engineers, particularly in marine and volcanic clays. Thixotropy, in engineering, may be defined as a loss of shear strength of a soil under load, with a time regain of strength upon removal of load. Some clays are very "thixotropic" and many other soils exhibit a similar quality, to a lesser degree, when remoulded. Thixotropy in clays is usually studied in the "gel system" form, consisting of a dense water suspension of clay. The loss of strength in thixotropy is commonly attributed to destruction of

adsorbed water orientation. Experiments tend to indicate this also. Moretto (1948) indicates thixotropic regain of strength is a function of the water content of the clay and possibly ion content. No regain was noted at the plastic limit while highest regain was at the liquid limit. Montmorillonites, which adsorb the most water, regain strength the most, with illites next, then kaolinite. Van Olphen (1951), in experiments with a Na bentonite suspension in water, indicated a decrease in regain of strength of the clay, with increasing concentration of Na salts up to a certain point, at which the regain strength increased sharply to a higher value than at initial concentration. The only explanation for this is in a sudden reversal of repulsive forces, due to interacting potentials between particles. A sharp increase in strength was noted also, with an increase in regain time.

Rosenquist (1953) discovered that marine clays originally deposited in salt water, but from which the salt had been leached, were extremely sensitive to remoulding. Loss of strength under load was complete. He also discovered, however, that the addition of a salt solution (Na) to the remoulded clay caused an immediate regain in strength. Some marine clays from which salt had been leached were stabilized by putting Na Cl into clay by means of electro osmosis.

Skempton (1952) also experimented with marine clay. He confirmed Rosenquist's results. Artificial leaching of salt from a marine clay made it sensitive and reintroduction of salt increased the strength. He attributes regain to orientation of adsorbed water.

Lambe (1953b) discusses thixotropy also.

Hirashima (1948) reports on physical character of a volcanic thixotropic clay. No determination of ions was made. The clay did have a low, 0.25, silica-sesquioxide ratio, which is typical of a tropical lateric soil. Base exchange capacity was high. Minerals were montmorillonite and illite, primarily.

The term, "silica-sesquioxide ratio", has been avoided until now, although the term is much used in soil work. It denotes the ratio of silica in a soil to the iron and aluminum content, expressed as oxides and is an indicia of the type of clay. The designation of a high silica-sesquioxide ratio usually is an indicia of a fairly high ion adsorption capacity. This is not always true, since a high degree of fine silt (and silicic acid) in a kaolin or illite clay, would give a high ratio which would be very misleading. Also, illite and montmorillonite, which have had silica replaced with Fe and Al, would give a low ratio and be misleading. Rapp (1940) conducted tests on the stability of asphalt surfaced roads on this basis by determining the

silica sesquioxide ratio and ions present. Roads with a
base course silica-sesquioxide ratio of over 1.7 or under
1.0 were unsatisfactory. In thise case, the higher ratio
soils, above 1.7, dusted readily in dry weather and were
plastic in wet weather.

In summary, it can be said that ions definitely do
affect the engineering properties of soil to varying degrees,
depending upon the minerals present, type of ion, and ion
water relationships.

Conclusions:

Sufficient evidence has been presented in the previous sections to conclusively illustrate that ions and ion exchange in a soil mass influence and alter to varying degrees, the engineering properties of the soil. The alteration of a soil mass by ions occurs during its geologic development and is influenced by the parent rock minerals, the mode of deposition, the climate, and ground water conditions. This period of development determines to a large extent the type of secondary soil minerals formed. In turn, the type of secondary mineral determines the extent of effect of ions upon the soil properties. This process of ionic exchange in soil masses is a dynamic process, continuing, never stable. In natural ionic exchange in soil, the time factor is such that only long term settlement might be affected from an engineering standpoint.

The ultimate goal in considering ionic exchange in soil masses is, of course, control of soil properties for engineering purposes by means of artificially induced ionic phenomena. The primary and immediate goal is a better understanding of the mechanisms and theory involved, to assist the soil engineer in properly evaluating and understanding the properties of the soil. This goal must be attained, and the basic science of soils understood before we can hope to intelligently modify or control soil properties. This approach is

little appreciated by many current investigators of artifi-
cial soil stabilization. This is evident in the method of
approach to the problem and in the failure to interpret
results. It is tacitly admitted by some.

In summary, we have shown that ions can alter soil
properties. The extent of effect is dependent upon the
composition of the soil mass and clay mineral present. The
effect of ions in most cases appears to be the influence of
ions upon the soil water surrounding the particles. The
degree of influence of ions upon the soil water is depend-
ent upon the particular ion. The action of a particular ion
is influenced by other ions and anions present. Organic
matter and the degree of decomposition influence ionic
effects. Bacterial action in soil will change both inorg-
anic and organic matter. The amount of soil water available
affects the degree of effect of the ions.

The basic workable theory of ionic structural relation-
ship to soil particles has been presented. In brief, it
consists of the soil particle to which is attached by
electrostatic bonds, a "fixed" layer of water of some struct-
ural network. Next to this fixed layer is a layer of ori-
ented water, varying in thickness and rigidity with the
type and amount of ion adsorbed in this layer, and the type
of clay mineral. It is suggested that the ions are also
within the fixed water structure, entering through the open

spaces between water molecules, and are in some cases, attached directly to the clay mineral surface. The type of ion entering the network is dependent upon ion size.

The exact nature of forces, and causes of variations of these forces, which bring about the orientation and fixation of water are not known.

It is apparent from this research that much investigation into the basic science and theory of ionic forces is required before a sound theory of ion-soil relationship can be postulated.

Recommendations for specific investigations necessary to further our knowledge of ions and soil are made in the next section.

It is believed that this investigation has pointed out some of the present lack of basic knowledge necessary in understanding soils. It is also believed that the material presented, has in a small way, contributed to a realization of the importance of a knowledge of basic soil science in evaluating soil properties in engineering.

The bibliography appended will be of assistance to future investigators of specific phases of ionic phenomena and soils.

RECOMMENDATIONS FOR FUTURE INVESTIGATIONS:

It has been apparent throughout the investigation, particularly in engineering properties research, that many specific projects are necessary to further our understanding of ion-soil relationships. The following outline of specific investigations is submitted as necessary to increase our knowledge of the subject.

I. Base Exchange Determination Technique

As noted previously, prior to undertaking any investigations involving determination of base exchange capacity, a method of determination must be decided upon. The commonly used potentiometric titration ⁻ is subject to error as noted in Grim (1953). A standard procedure should be determined for engineering use in testing soils. A complete survey of existing literature, of which there is a great deal, must be made and specific methods checked before establishing standards. Microchemical methods recently developed are also subject to error. Suggested references are: all Soil Science papers, Kelley (1948), Grim (1953), Lutz (1948), Am. Potash (1948), and other references in the above books. NOTE: Exchange capacity pH should always be stated.

II. Anion Exchange Determination Technique

Little has been done on anion exchange and much

information is needed. A standard method must again be selected . Suggested references are Grim (1953), Vol. 59 Soil Science. These refer to others.

III. Anion Exchange Capacity of Clay Minerals

The effect of type of clay mineral and particle size of mineral must be determined for various inorganic anions commonly used. Grim (1953) and Soil Science. Multiple valence of some anions (Cl) may have effect.

IV. The Effect of Anions on Engineering Properties of Soil

Little is known about this. Determine the effect of various anions on the properties of clay minerals using a single cation such as sodium. Use Atterberg limits as test. Reference Holmes, Roediger, Wirsig and Snyder (1943) and Soil Science; also attached bibliography.

V. The Effect of Clay Mineral Particle Size Upon Base Exchange Capacity

Determine the base exchange of equivalent weights of different particle size of each clay mineral group using a single cation salt. Such an exact determination has not been plotted. Suggest oil centrifuge fractionation of sample.

VI. Determination of the Effect of Ions Upon the Dry
     Strength and Shrinkage of Clay Minerals

Use several cations and one mineral at a time.
Determine grain sizes. Saturate with ions. Determine
crushing strength and shrinkage limit of each sample,
oven dried at a given temperature. Oven humidity should
be checked. Lambe (1953). This may help understand
ionic forces.

VII. Determination of Ionic Adsorbed Water Film Strength

Use Na ion and single clay mineral montmorillonite.
Saturate with Na. Take samples from batch at time inter-
vals. Determine water content and consolidate specimen.
Plot water content as function of time and void-ratio
pressure curve. Correlate slope of curves to determine
effect of pressure and water content as an indicia of
adsorbed oriented water film strength by resistance to
consolidation. Deduct osmotic force. Salas and Serra-
tosa (1953).

VIII. The Effect of Ions on Apparent Particle Size Analysis

Due to formation of flocs, the particle size deter-
mined by mechanical analysis is not always a good indicia
of true size. Some work has been done on the (see refer-
ences noted under discussion of flocculation), but more is
necessary. Check silt and clay or ground quartz and clay

mineral mixtures. Saturate with various ions, single
anion, and determine particle size change by mechanical
analysis.

IX.   The Effect of Iron and Aluminum on Ion Adsorption

Select iron free clay mineral or remove iron (see
appended references), saturate with ions, attempt to
exchange Fe and Al, check exchange capacity. Attempt to
resaturate with original ion and compare difference in
adsorption.

X.   The Effect of Ions and Anions on Silica Solubility

Silica gels derived from fine silt often mask ionic
exchange reactions by adsorbing ions. Determine effect of
of common soil ions and anions on silica (quartz) solubi-
lity in fine particle size.

XI.   The Effect of Anions on Cation Exchange Capacity

Use single cation, several anions. Determine change
in exchange capacity caused by different anions. Use a
single particle size clay mineral.

XII.   The Effect of Ions on Liquid Adsorption on Clay
       Minerals

Reference Winterkorn and Baver (1934). Much extension
of this work necessary.

XIII.   The Effect of Ions on Soil Colloid Gel Volume

Use given particle size of clay mineral. Use given
weight of sample dried for given period and temperature.
Use same weight for each sample, with different ion.

Stir suspension of ion saturated dry sample in water.
Determine volume after given time. Volume will be indicia
of adsorbed water layer thickness.

XIV. The Effect of Ions upon Soil Permeability

Use single clay mineral of known particle size distri-
bution. Determine permeability with various ions. Mech-
anism is one of adsorbed water thickness and flocculation
and dispersion.

XV. The Effect of Ions Upon the Stability of "Quick Silts"

Determine silt particle size exchange capacity. Deter-
mine ion effects on stabilizing or reducing "quick" condi-
tions. May be none due to water overuling ion effect.
Try using Na clay as an additive to silt.

XVI. The Migration of Soil Ions

Use radioactive ions (Ca). Put given quantity in
natural soil mass and determine migration of ions with
time and weather conditions. Use counter to check
migration.

Many other investigations will be suggested from the
above brief list. Others suggested are: the effect of
organic ions on Atterberg limits, organic ion adsorption,
change in adsorbed water properties with increase in ion
concentration noted previously by sudden increase at high
Na concentration.

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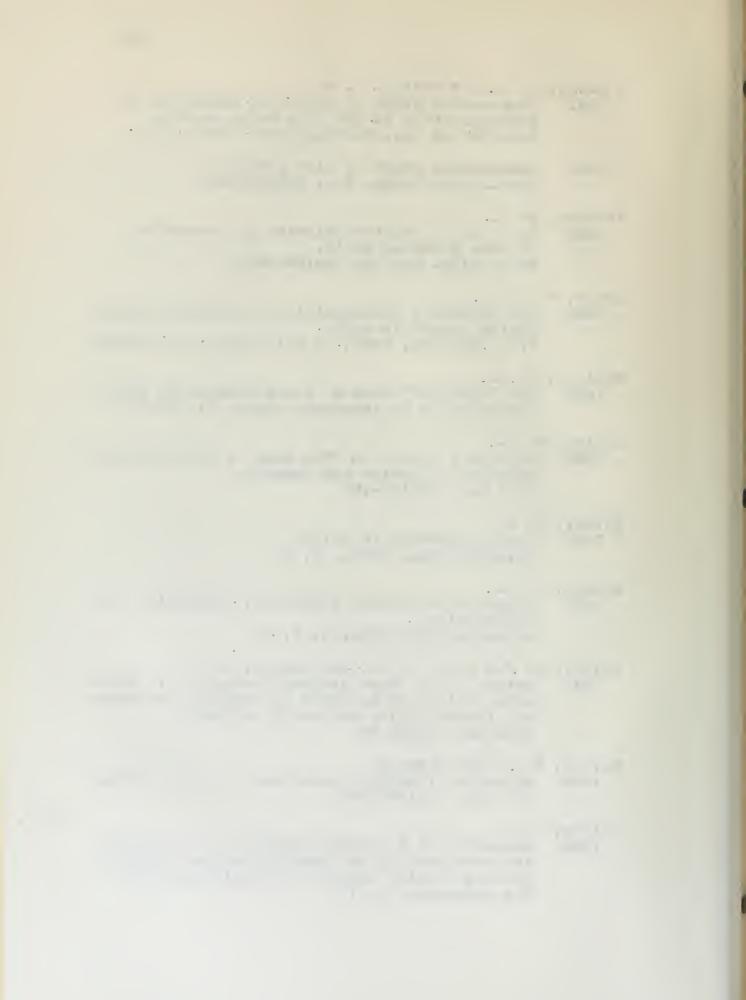   1941   Fundamental study of clay: II. Mechanism of
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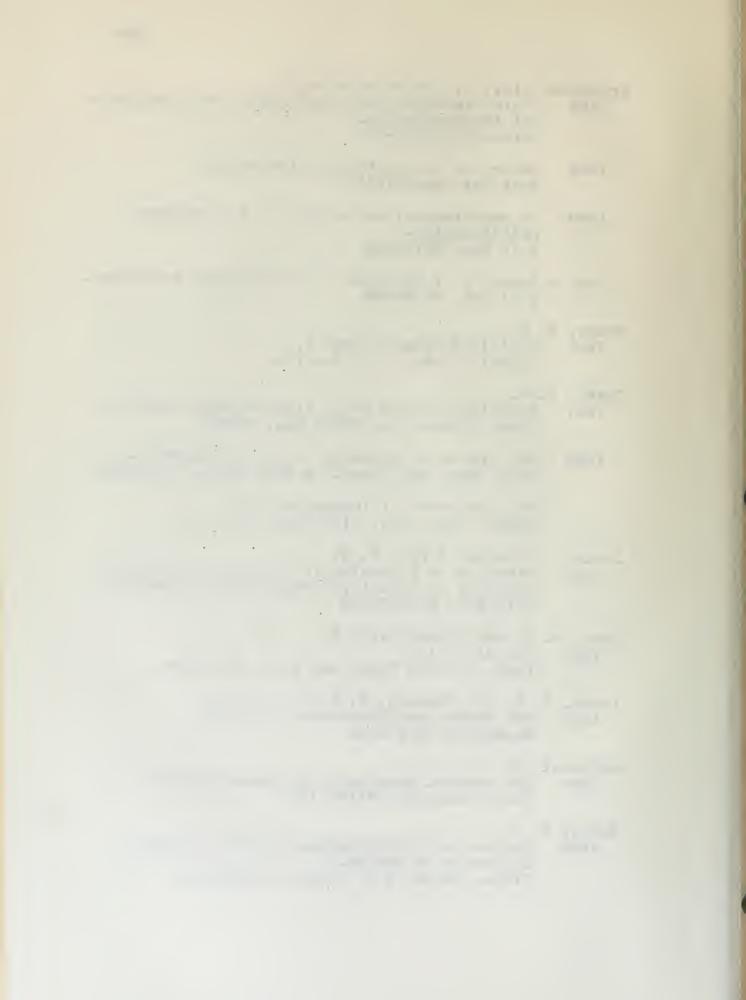   New Brunswick, N. Y.

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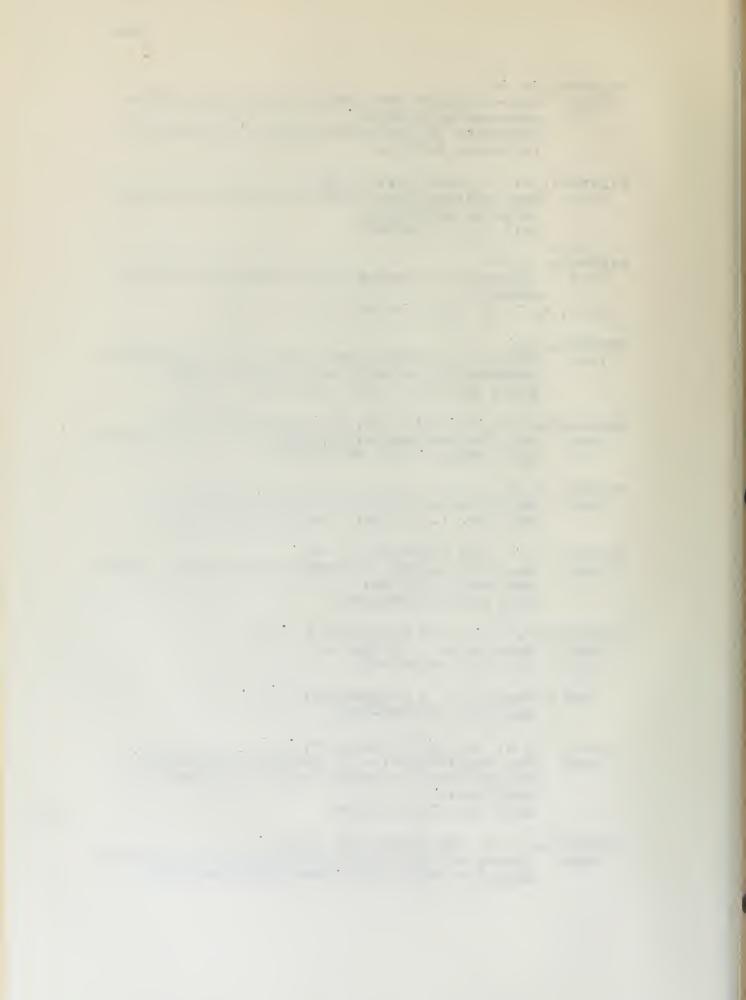   Abstracts of Doctorate Thesis, University of
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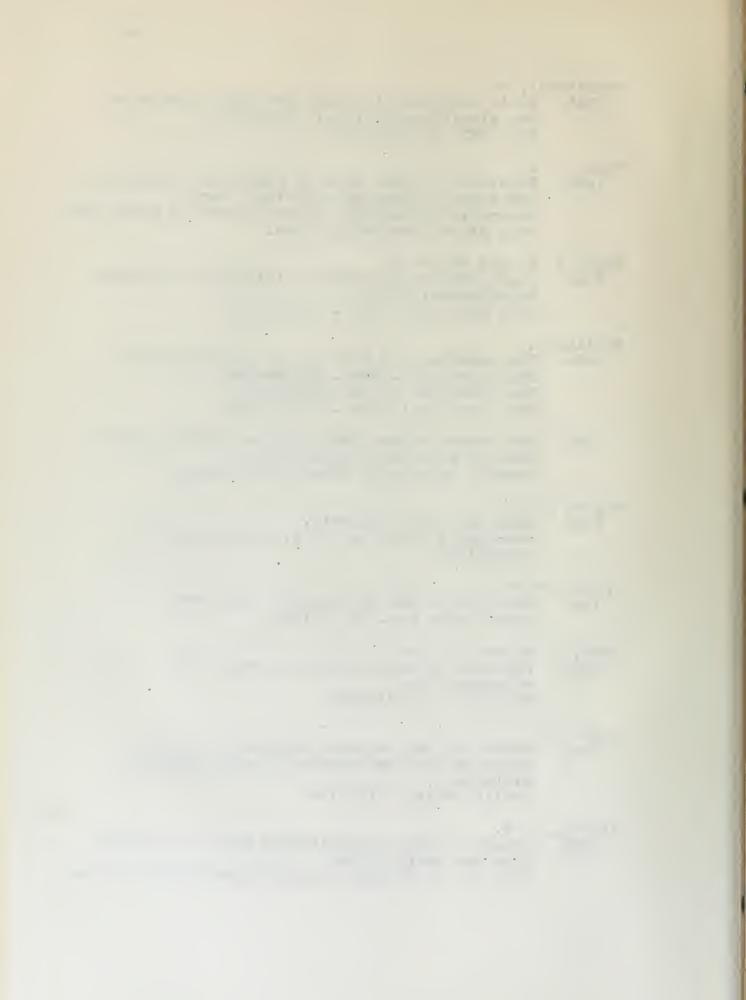
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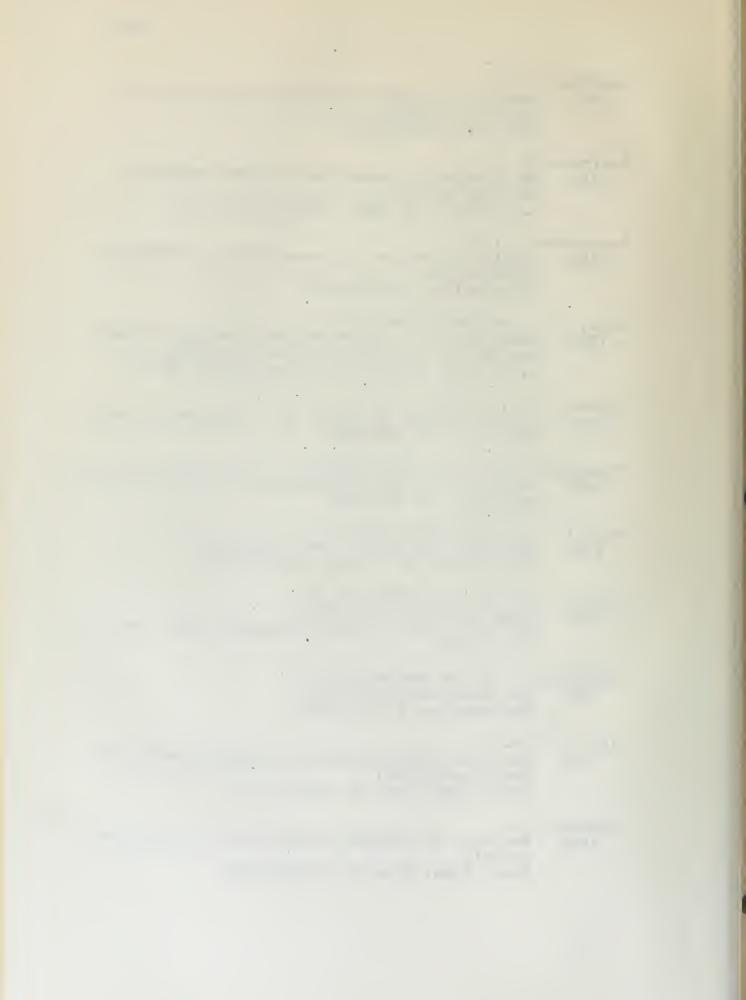   Jour. Amer. Soc. Agron. 20:354-373.

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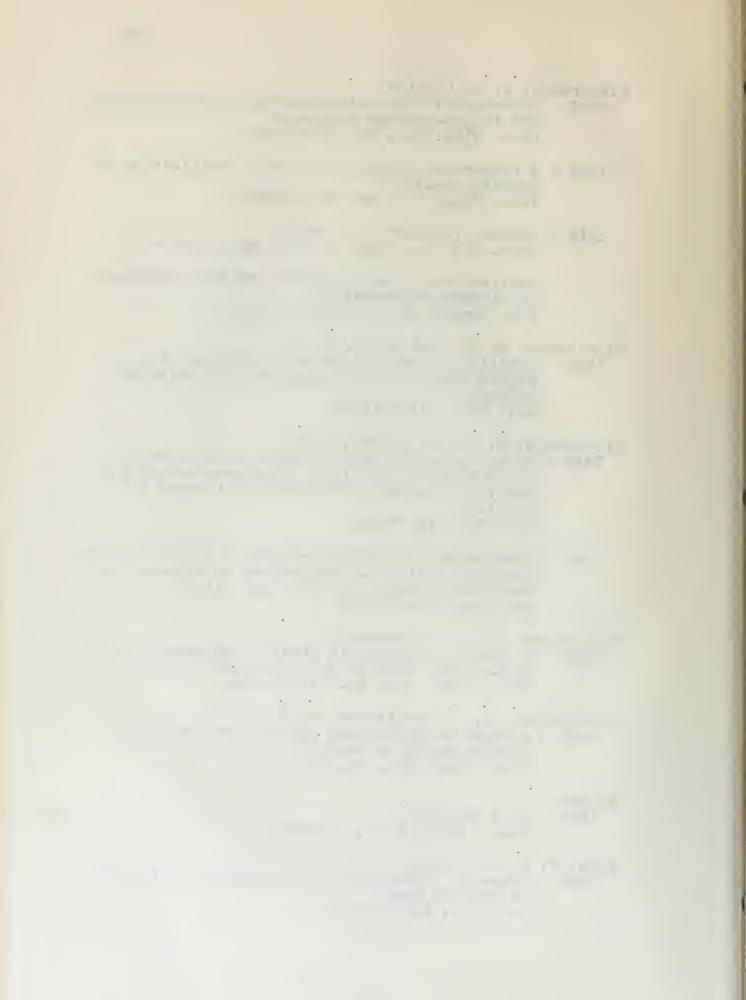   cohesive soils.
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